

HEAT TRANSFER IN REACTING GAS MIXTURES  
WITH LARGE PRESSURE GRADIENTS

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Gerald Albert Marxman

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## ABSTRACT

Energy transport by conduction and diffusion is considered in chemically-reacting, gaseous mixtures which have a pressure gradient parallel to the temperature gradient. As a consequence of pressure diffusion and other mechanisms, the pressure gradient can influence energy transport, and this effect is given particular emphasis. The use of an idealized flow model and a perturbation technique makes it possible, with a relatively simple analysis, to deduce many of the features of energy transport in multicomponent, gaseous media.

The dissociation reaction of a diatomic gas, with the ratio (reaction rate/diffusion rate) either large or small, is studied. When the flow is chemically frozen, the extension of the analysis to include any number of components would be straightforward, in principle. However, when the gas is in local chemical equilibrium, the binary case is unique in that the diffusion velocities are then proportional to the local temperature gradient, but independent of the local pressure gradient. Consequently, there exists an effective thermal conductivity. The order of the governing set of equations is therefore the same as for a simple, single-component gas, and the effect of the wall surfaces on reaction rates is confined to reaction boundary layers. Two other examples illustrate that the order of the equations is higher when the equilibrium flow comprises more than two components, although there are still reaction boundary layers. The additional boundary conditions associated with the higher order are determined, through integral conditions, by the proportions of the chemical elements present.

The results show that in many high-temperature gasdynamics problems of current interest the presence of a pressure gradient may have an important influence on energy transport.

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## I. INTRODUCTION

The temperatures encountered in many gasdynamics problems of current interest are high enough to induce extensive dissociation, and sometimes ionization, of the gas molecules. As a consequence, it has become necessary to consider the influence of chemical reactions within the gas and interdiffusion among the various species present. When dissociation is present, the accompanying diffusion processes provide an energy transport mechanism which supplements the ordinary conductive heat transfer, and it is this diffusive energy transport and associated effects which will be of particular interest in the present work.

In recent years several problems concerned with energy transport in hot gases where diffusion plays a role have been discussed in papers by a number of authors. One such problem which is of considerable practical interest arises in connection with the recovery of space vehicles when they return to a planetary atmosphere at hypersonic speeds. Elevated temperatures are generated in the re-entry process, because nearly all of the enormous kinetic energy of the vehicle must be dissipated in the form of heat. When the hypersonic, blunt-nosed body penetrates the atmosphere, the surrounding flow exhibits a bow shock wave, a layer of dissociated and ionized hot gas between the shock wave and the body, and a "boundary layer" over the surface. Heat energy is transferred through the boundary layer to the vehicle primarily by thermal conduction and diffusion processes, and also by radiation from the layer of hot gas. Various aspects of the heat transfer problem in the dissociated boundary layer

have been studied by Reshotko and Cohen (1),\* Lees (2), Denison and Dooley (3), Fay and Riddell (4), and others.

Other authors have considered similar problems from a somewhat different viewpoint, in an effort to provide a better understanding of the details of the solution, such as composition profiles and the influence of catalytic wall surfaces, as well as the associated heat transfer effects. Hirschfelder (5) has studied diffusion and energy transport processes in a reacting gas which is in local chemical equilibrium and is at rest, confined between two parallel plates at different temperatures. Clarke (6) considered a dissociated diatomic gas, also in local chemical equilibrium, but in a Couette flow. In an effort to show at least qualitatively the effect of varying the chemical reaction rates, Broadwell (7) has adopted a simple, linear approximation to replace the complicated, non-linear, reaction-rate law, or law of mass action. Using this approximation, Broadwell studied the motionless dissociating gas, a Couette flow, and a boundary layer flow. His analysis provides some insight into the general behavior of the energy transport, composition profiles, and temperature profile as the gas shifts from the chemically frozen regime to a state of local chemical equilibrium.

One feature shared by all of these flow models is the absence of a pressure gradient in the direction of energy flux and diffusion. Consistent with this, it has been common practice to describe the diffusion process mathematically by means of the well-known Fick's law, which treats the concentration gradients as the sole driving forces for diffusion.

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\* Numbers in parentheses designate references listed at the end of the text.

On the other hand, the kinetic theory of gases shows that in general there are two other driving forces. If the molecular masses of the diffusing species are unequal, there is a tendency for the heavier particles to diffuse toward a region of higher pressure, while the lighter particles tend to diffuse toward a region of lower pressure. This phenomenon is generally called "pressure diffusion". In addition, a diffusion flux can also arise as a result of a temperature gradient; this is usually termed "thermal diffusion". However, when there is appreciable concentration diffusion and pressure diffusion, thermal diffusion is ordinarily negligible.

The diffusion currents due to pressure gradients are not so clearly negligible. In fact, pressure diffusion plays a significant role in the atmosphere, for example, and may be important in many physically interesting flow problems. Any flow with curved streamlines will have a pressure gradient normal to the streamlines, leading to the possibility of pressure diffusion if two or more components are present. Among the simplest examples are the cylindrically-symmetric, rotating flows with high tangential velocities, in which there is a radial pressure gradient.

Of particular current interest is the vortex flow of very high temperature gases, which is receiving much attention as the basis for a magnetohydrodynamic power generator (8), for example. In this device, power is extracted from a hot, partially ionized gas spiralling inward through an axial magnetic field between two concentric, cylindrical electrodes. Kerrebrock and Meghreblan (9) have shown that the vortex also has potential as a containment mechanism for a gaseous fission rocket. Their study indicated that it may be possible to retain the heavy fissionable material, in gaseous form, in the pressure field of a vortex, while the low-molecular-weight propellant diffuses radially inward through it.

This would enable the direct transfer of energy from the fissioning gases to the propellant, through radiation and molecular collisions, without the interposition of any solid surface.

It is clear that in these applications, and in others of a similar nature, the energy transport may be strongly influenced by the pressure gradient, through the mechanism of pressure diffusion and by means of other less direct effects on the chemical reactions. To learn more about the magnitude of this influence, the author and Kerrebrock (10) considered a vortex flow of a dissociating, diatomic gas in local chemical equilibrium between concentric, porous cylinders which rotate with the flow. The non-linear equations corresponding to this system were programmed for a digital computer, and selected calculations were performed for the specific example of oxygen dissociation. The results showed that for given temperature boundary conditions, the energy transport is quite sensitive to the tangential Mach number of the vortex, even when the degree of dissociation is quite small. The Mach number is a measure of viscous dissipation as well as of the pressure gradient, of course, but only a small part of the effect can be attributed to the former. It was also found that even very small radial flows through the walls, corresponding to Reynolds numbers of the order of one, have a large effect on the energy transport, especially when dissociation is present. This can be anticipated, because a convection current acts in essentially the same way as the diffusion mechanism in transporting energy.

The objective of the present work is to achieve a better understanding of diffusive energy transport processes in chemically-reacting gas flows which incorporate pressure gradients. The analysis is carried

out within the framework of a flow model which may be considered as a limiting case of the vortex; the flow is assumed to be constrained between concentric cylinders whose radii of curvature greatly exceed the separation distance. This "channel-flow approximation" effects a considerable simplification in the mathematical formulation of the problem, and by putting suitable restrictions on chemical parameters such as reaction rates and equilibrium constants, it is possible to obtain analytical solutions. The limitations imposed by these approximations are not a handicap to describing the qualitative behavior of the solution, although quantitative results based on the analysis are not strictly suitable for every situation of interest. However, even "exact" solutions, which could only be obtained numerically, might be of somewhat limited quantitative value in some cases, due to the present indefinite knowledge of certain parameters, such as chemical reaction rates. In view of this, the advantages associated with the analytical solutions seem to more than justify the approximations employed to obtain them.

In the following section the basic features of the theory of transport processes in gases are outlined. There are two approaches to this theory, and both are discussed. One of these, kinetic theory, may be classified as "microscopic" in character, while the other method, irreversible thermodynamics, is a "macroscopic" approach. Both methods lead to the same phenomenological form for the transport equations, although only kinetic theory is capable of a truly complete formulation of the problem; the coefficients in the equations depend on the details of the collisions between the particles, which must be studied on a microscopic basis. However, only the phenomenological form of the equations will be

required for the analytical work of the subsequent sections, and no consideration will be given to the details of collision dynamics.

## II. DIFFUSION AND ENERGY TRANSPORT IN GASES: THE MATHEMATICAL FORMULATION

There are currently two basic methods of studying transport phenomena in gases. A great deal of success in understanding these non-equilibrium processes has been achieved through the application of statistical principles to provide a theory of non-equilibrium statistical mechanics, usually called "kinetic theory". Although the kinetic theory is generally regarded as a separate subject, complete in itself, in a broad sense it can be thought of as an extension of equilibrium statistical mechanics to include non-equilibrium phenomena. More recently, a second means of considering these phenomena has been formulated. This thermodynamic theory of irreversible processes is an extension of the principles of classical thermodynamics to include non-equilibrium, or irreversible processes. Thus, in a general way, irreversible thermodynamics bears the same relationship to kinetic theory as does classical thermodynamics to equilibrium statistical mechanics; the two methods of treating irreversible processes in gases and gaseous mixtures are complementary, each having its merits and shortcomings.

It will be the purpose of this section to briefly review the important features of kinetic theory and irreversible thermodynamics, as applied to transport processes in gases, and to summarize the results needed for the analysis to follow.

### The Kinetic Theory of Gases

Maxwell, Boltzmann, and others first used statistical methods to study transport properties in dilute gases about a century ago, and the development of modern kinetic theory since then has been associated with



the work of these men as well as the more recent contributions of Chapman, Enskog, and others (11, 12). The book by Chapman and Cowling (11) devotes one section to an interesting history of the development.

The theory for a binary mixture of gases is given an elegant presentation by Chapman and Cowling, and the extension to a multicomponent mixture is contained in the book by Hirschfelder, Curtiss, and Bird (12). In the summary of the results of kinetic theory to follow, the notation of the latter will be followed closely in most cases.

To describe the exact dynamical state of a system of particles, it is necessary to prescribe the momentum and position coordinates at a given time. If this is done, it is possible to predict exactly the dynamical state at any future time, according to the laws of classical mechanics. Of course, it is a practical impossibility to give the exact state of so complex a system as a gas, and this leads to the use of statistical methods. In kinetic theory, it is shown that the macroscopic properties of a dilute gas can be accurately described in terms of a distribution function,  $f(\underline{v}, \underline{r}, t)$ . The distribution function is defined so that  $f(\underline{v}, \underline{r}, t) d\underline{r} d\underline{v}$  is the probable number of molecules having at time  $t$  position coordinates between  $\underline{r}$  and  $\underline{r} + d\underline{r}$  and a velocity between  $\underline{v}$  and  $\underline{v} + d\underline{v}$ . The mathematical basis for the kinetic theory of gases is the Boltzmann equation, an integro-differential equation which specifies the distribution function. The Boltzmann equation involves complex "collision integrals" which account for the effect of binary collisions on the distribution function, and it is valid only for densities low enough so that three-body collisions are unimportant.

If conditions are such that the gas behaves like a continuum, i. e.

if the mean free path is much less than the characteristic physical dimension of the system, the hydrodynamic equations of conservation of mass, momentum, and energy can be derived from the Boltzmann equation without solving explicitly for the distribution function. In the course of this derivation the fluxes of mass, momentum, and energy are identified with integrals involving the distribution function. These fluxes are, of course, directly related to the diffusion velocity, pressure tensor, and energy transfer. Thus one can represent these latter quantities in the following symbolical manner:

$$u_j(r, t) = \int g_1(f_j) dV_j \quad (1)$$

$$P(r, t) = P\left( \int g_2(f_j) dV_j \right) \quad (2)$$

$$Q(r, t) = Q\left( \int g_3(f_j) dV_j \right) \quad (3)$$

where  $P$  and  $Q$  are the pressure tensor and flux of kinetic energy, respectively, and functions of the indicated integrals;  $g_1$ ,  $g_2$  and  $g_3$  are functions of the distribution function.

The diffusion velocity of species  $j$  is defined by:

$$u_j(r, t) = V_j - V_o \quad (4)$$

where  $V_j$  = average velocity of species  $j$  relative to a fixed coordinate system,

$$V_o = \text{mass average velocity} = \frac{1}{\rho} \sum M_j V_j .$$

For later reference the hydrodynamic conservation equations, derivable from the Boltzmann equation as previously stated, will be listed here. In the presence of chemical reactions the continuity equation for

the  $j^{\text{th}}$  species is:

$$\frac{\partial n_j}{\partial t} + \nabla \cdot n_j (V_o + u_j) = K_j \quad (5)$$

$K_j$  is the rate of production of  $j$  in moles/cm<sup>3</sup> - sec due to chemical reactions. Since total mass in the system is conserved,

$$\sum m_j K_j = 0 \quad (6)$$

where  $m_j$  = molecular weight of species  $j$ . Multiplying equation 5 by  $m_j$  and summing therefore leads to the familiar continuity equation of fluid mechanics:

$$\frac{\partial \rho}{\partial t} + (\nabla \cdot \rho V_o) = 0 \quad (7)$$

The equation of motion is:

$$\frac{\partial V_o}{\partial t} + (V_o \cdot \nabla) V_o = -\frac{1}{\rho} (\nabla \cdot P) + \frac{1}{\rho} \sum n_j F_j \quad (8)$$

where  $P$  is the pressure tensor and  $F_j$  is the external force per unit mass acting on species  $j$ .

The energy equation is:

$$\rho \left[ \frac{\partial e}{\partial t} + (V_o \cdot \nabla) e \right] = -\nabla \cdot Q - (P : \nabla V_o) + \sum n_j (V_j \cdot F_j) \quad (9)$$

where  $e$  is the thermodynamic specific internal energy of the gas, and does not include the kinetic energy associated with  $V_o$ , nor the potential energy associated with  $F_j$ .  $Q$  is the energy-flux vector.

Although these conservation equations are valid under any circumstances in which the concept of a fluid continuum is applicable, it is not possible to obtain simple expressions for  $u_j$ ,  $P$ ,  $Q$ , and  $K_j$ , which are the non-equilibrium or irreversibility factors in the equations. The primary concern of kinetic theory is in obtaining approximate solutions to

the Boltzmann equation so that the diffusion velocity, pressure tensor, and heat flux can be expressed in terms of the macroscopic thermodynamic variables, using the equations represented symbolically by equations 1, 2, and 3. (The reaction rate  $K_j$  is given by chemical kinetics.)

If a gas mixture is allowed to achieve chemical, thermodynamic, and mechanical equilibrium, so that no irreversible processes are occurring, the distribution function will be locally Maxwellian. This is expected from the viewpoint of equilibrium statistical mechanics, which applies in this case, and it can also be shown to follow from the Boltzmann equation for this special case. Anticipating that the distribution function might not be radically changed from the local Maxwellian distribution when irreversible processes of a physically interesting magnitude are present, Enskog obtained an approximate solution to the Boltzmann equation using a perturbation technique. (Chapman independently arrived at the same result by a more intuitive and less mathematically rigorous means.) Enskog introduced an expansion parameter  $\sigma$ , where  $1/\sigma$  is a measure of the frequency of collisions. Thus if  $\sigma$  is extremely small, collisions are very frequent and the gas mixture achieves local equilibrium everywhere. The distribution function for the  $j^{\text{th}}$  species, for example, is expanded in the series:

$$f_j = f_j^{(0)} + \sigma f_j^{(1)} + \sigma^2 f_j^{(2)} + \dots$$

The zeroth-order term is the locally Maxwellian distribution function, and the hydrodynamic conservation equations which correspond to this term alone are the Eulerian equations. Addition of the first-order correction leads to the Navier-Stokes equations. Higher order approximations are of less interest here and will not be considered.

When this series is substituted into the Boltzmann equation, a set of integro-differential equations is obtained for each of the functions  $f_j^{(0)}$ ,  $f_j^{(1)}$ . The equations for  $f_j^{(0)}$  correspond to equilibrium and  $f_j^{(0)}$  is the Maxwellian function, as already mentioned. The solution for  $f_j^{(1)}$  has been obtained by Chapman and Cowling (11) in terms of a rapidly converging series of Sonine polynomials.

By introducing the resulting approximate solution for the distribution functions into the expressions represented by equations 1, 2 and 3, it is found that the diffusion velocity, pressure tensor, and heat flux can be expressed in terms of the thermodynamic variables. The diffusion velocity  $u_i$  of species  $i$  can be written:

$$u_i = \frac{n_i^2}{n_i \rho} \sum_{j \neq i} m_i \mathcal{D}_{ij} d_j - \frac{1}{n_i m_i} \alpha_i \nabla \ln T \quad (10)$$

where

$$d_j = \nabla \left( \frac{n_j}{n} \right) + \left( \frac{n_j}{n} - \frac{n_j m_j}{\rho} \right) \nabla \ln p - \frac{n_j m_j}{\rho p} \left( \frac{\rho}{m_j} F_j - \sum_k n_k F_k \right) \quad (11)$$

The  $\mathcal{D}_{ij}$  are the multicomponent diffusion coefficients, and the  $\alpha_i$  are the thermal diffusion constants for the mixture. These will be discussed later.

Equation 10 shows that under the conditions implied by the Chapman-Enskog approximation, the diffusion velocity is proportional to the concentration gradient, pressure gradient, difference in the external forces acting on the different species of molecules, and temperature gradient. The last effect, called thermal diffusion, was unknown theoretically and experimentally prior to the work of Chapman and Enskog. Subsequently, experiments showed that the predicted thermal diffusion does

occur, and this constituted a major verification of the kinetic theory.

It is sometimes convenient to express the diffusion velocity in a multicomponent mixture in terms of the binary diffusion coefficients,  $D_{ij}$ , which are practically independent of the composition, unlike the multicomponent diffusion coefficients,  $\mathcal{D}_{ij}$ . (The  $\mathcal{D}_{ij}$  are defined so that they reduce to the  $D_{ij}$  in the case of a binary mixture.) If this is done the result is:

$$\sum_i \frac{n_j n_i}{n^2 D_{ji}} (u_i - u_j) = d_j - \nabla \ln T \sum_i \frac{n_j m_j \alpha_i - n_i m_i \alpha_j}{n^2 m_i m_j D_{ji}} \quad (12)$$

The pressure tensor which is obtained from the Enskog solution together with the equation represented by equation 2 can be written:

$$P = p(1) - \mu \left[ \nabla V_0 + (\nabla V_0)^+ - \frac{2}{3} (\nabla \cdot V_0)(1) \right] \quad (13)$$

where (1) is the unit tensor and the symbol + indicates the transpose tensor obtained by interchanging rows and columns. The coefficient  $\mu$  is called the coefficient of viscosity, and  $p$  is the static, or "thermodynamic", pressure.

Similarly, equation 3 leads to:

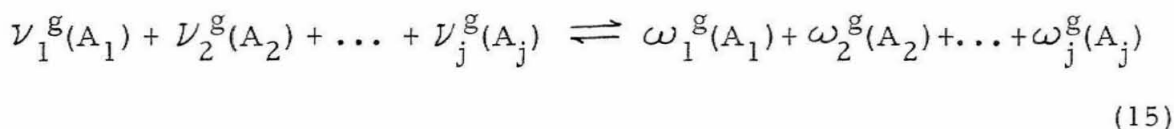
$$Q = - \lambda \nabla T + \sum_i n_i h_i u_i - \frac{kT}{n} \sum_{ik} \frac{n_k}{m_i D_{ik}} \alpha_i (u_k - u_i) \quad (14)$$

where  $h_i$  is the enthalpy per mole of species  $i$ ,  $\lambda$  is the thermal conductivity, and  $k$  is Boltzmann's constant. This is a generalization of Fourier's law of heat conduction. The first term gives the heat transferred by thermal conductivity, and the second is the flux of energy carried by the diffusion process. The last term is usually very small and is an

interference, or cross-effect with diffusion, somewhat analogous to the effect of a temperature gradient on diffusion, i. e. thermal diffusion (which is also usually a small effect).

The detailed dynamics of the collisions between molecules of the various species enter in the evaluation of the transport coefficients,  $D_{ij}$ ,  $\alpha_i$ ,  $\mu$ , and  $\lambda$ . The Enskog solution for the first-order perturbation leads to equations for the transport coefficients in terms of the Sonine polynomial expansions, but the expansion coefficients are complicated functions of collision integrals, and these depend on the intermolecular force laws between all types of molecules present. No effort will be made here to discuss the elaborate calculations which workers in kinetic theory such as Hirschfelder, et al (12) (Chapter 8), have performed to obtain the transport coefficients. However, considerable success has been achieved in this direction, and the results are generally in excellent agreement with experimental values for the gases with relatively simple molecular structures.

The remaining irreversibility factor,  $K_j$ , which is the rate of production of species  $j$  by chemical reactions, is given by the law of mass action, discussed in textbooks on chemical kinetics (13). The kinetics of the reacting mixture can be represented by a set of stoichiometric equations of the form:



The  $\nu_j^g$  and  $\omega_j^g$  are the stoichiometric coefficients of reaction  $g$  and are integers. The symbol  $(A_j)$  denotes the chemical formula of the  $j^{\text{th}}$  species. The forward reaction rate in the  $g^{\text{th}}$  reaction is then:

$$k_f^g(n_1)^{\nu_1^g}(n_2)^{\nu_2^g} \dots (n_j)^{\nu_j^g}$$

and the backward reaction rate is:

$$k_b^g(n_1)^{\omega_1^g}(n_2)^{\omega_2^g} \dots (n_j)^{\omega_j^g}$$

where  $k_f^g$  and  $k_b^g$  are the forward and backward rate constants for reaction  $g$ , respectively, and  $n_j$  is the molar concentration of species  $j$ . The total rate of production of  $j$  is then:

$$K_j = \sum_g (\omega_j^g - \nu_j^g) \left[ k_f^g(n_1)^{\nu_1^g}(n_2)^{\nu_2^g} \dots (n_j)^{\nu_j^g} - k_b^g(n_1)^{\omega_1^g}(n_2)^{\omega_2^g} \dots (n_j)^{\omega_j^g} \right] \quad (16)$$

The mathematically rigorous kinetic theory of transport processes based upon the Boltzmann equation is extremely powerful, providing not only the correct generalizations of familiar phenomenological laws such as Fick's law of diffusion and the Fourier law of heat conduction, but also the means by which the transport coefficients appearing in those equations can be evaluated, at least in principle. Perhaps the chief shortcoming of the theory is that it affords little clarification of the physical mechanisms underlying the phenomena. A better physical understanding can be obtained by following closely the microscopic processes which result in diffusion, heat conduction, and viscous effects. With this approach it is possible to "derive", in a manner of speaking, many of the important terms in equations 10, 13, and 14, but of course without the mathematical exactness of the Chapman-Enskog solution. In his book, Jeans (14) uses this method to provide a clear discussion of concentration



diffusion (i. e. diffusion due to the first term on the right-hand side of equation 11), viscosity, and ordinary heat conduction (given by the first term on the right-hand side of equation 14).

The logic behind this approach is quite simple. For example, consider concentration diffusion. Suppose a binary gaseous mixture of species A and B has a composition which depends only on the  $z$ -coordinate; for definiteness, the concentration, or number density of A increases with increasing  $z$  while that of B decreases. Because of their thermal motion, some fraction of the molecules of A contained in the space corresponding to a mean free path on either side of the plane  $z = z_0$  will cross that plane in a given time interval. However, since the average number density of A molecules above the plane is greater than that below, there will be more molecules crossing the plane in a downward direction than in the opposite direction. Thus, there is a net mass flux, or diffusion, of species A away from the region of higher concentration. The same is true of the B molecules, of course, so that in this example the two species undergo concentration diffusion in opposing directions. This non-equilibrium process will continue until equilibrium has been achieved, i. e. until the concentrations of A and B are uniform.

Viscosity and heat conduction can be explained by similar arguments. In treating the former the discussion is quite analogous to that for concentration diffusion, except that the quantity which varies with  $z$  is the mean momentum of the molecules rather than the concentration. Thus, while diffusion is a transport of mass, viscosity is a transport of momentum. Heat conduction is, of course, a transport of energy, and the  $z$ -dependent variable in the argument is the mean thermal energy of

the molecules. These elementary and mathematically inexact treatments of transport processes, which are valuable primarily for the physical understanding they provide, are generally well known and need not be pursued further here.

### The Mechanism of Pressure Diffusion

Less attention has been given to providing a lucid explanation of the physical mechanism of pressure diffusion (the second term on the right-hand side of equation 11). Since the effects of a pressure gradient are to be considered in subsequent sections, it seems worthwhile to present a brief mechanistic discussion of pressure diffusion here. To do this as simply as possible, consider a binary gas mixture comprising a heavy and a light species, whose molecules have mass  $M$  and  $m$ , respectively. Disregarding viscous effects, and assuming that the only external forces acting are body forces (i. e. forces proportional to mass, such as the force due to gravity), the macroscopic, steady-state equation of motion obtained from equation 8 is:

$$(\mathbf{V}_0 \cdot \nabla) \mathbf{V}_0 = - \frac{1}{\rho} \nabla p + \mathfrak{F} \quad (17)$$

where  $p$  is the static pressure and  $\mathfrak{F}$  is the body force. Next, consider the equations of motion for the individual molecules. It will be convenient to write these equations in a coordinate system which is moving with the local velocity and acceleration of the gas mixture. Accordingly, the equation of motion of a heavy molecule (species 1), valid at some point  $x, y, z$  of a stationary coordinate system, but written in terms of a coordinate system moving with the flow at that point, is

$$M \frac{d\mathbf{V}_1}{dt} = \mathbf{F}_b + \mathbf{F}_c - M \frac{d\mathbf{V}_0}{dt}$$

or

$$M \frac{dV_1}{dt} = F_b + F_c - M(V_o \cdot \nabla) V_o \quad (18)$$

where  $V_1$  is the velocity of the molecule of mass  $M$  relative to the mass-average flow,  $F_b$  is the body force acting on the molecule, and  $F_c$  is the average force due to collisions. The average collision force should be proportional to the velocity of the molecule relative to the flow  $V_1$ , an effective collision cross-section  $\sigma$ , the average concentration of particles of both kinds  $n$ , the mean thermal velocity  $\bar{c}$  of the particles, and some complicated function of the average momenta  $f(\bar{mc})$  which depends on the detailed dynamics of the collisions and accounts for the average exchange of momentum in a collision. Thus:

$$F_c = V_1 \sigma n \bar{c} f(\bar{mc}) = V_1 \sigma n \sqrt{\frac{3kT}{m}} f(\bar{mc}) \quad (19)$$

where the proportionality factor is absorbed in  $f(\bar{mc})$ . Furthermore, the body force is

$$F_b = M \tilde{\mathcal{F}} \quad (20)$$

By combining equations 17, 18, 19 and 20 one obtains:

$$M \frac{dV_1}{dt} = V_1 \sigma n \sqrt{\frac{3kT}{m}} f(\bar{mc}) + M \tilde{\mathcal{F}} - M(V_o \cdot \nabla) V_o$$

or

$$M \frac{dV_1}{dt} = V_1 \sigma n \sqrt{\frac{3kT}{m}} f(\bar{mc}) + \frac{M}{\rho} \nabla p \quad (21)$$

Similarly, for the light molecules:

$$m \frac{dV_2}{dt} = V_2 \sigma n \sqrt{\frac{3kT}{m}} f(\bar{mc}) + \frac{m}{\rho} \nabla p \quad (22)$$

Assuming that the acceleration of the particles relative to the moving coordinate system is small and can be neglected ( $dV_1/dt \approx 0$ ,  $dV_2/dt \approx 0$ ), then subtracting equation 22 from 21 and averaging over a large number of particles (since the diffusion velocities are by definition  $u_1 = \overline{V}_1$  and  $u_2 = \overline{V}_2$ ):

$$u_1 - u_2 = g(p, T, n_1, n_2, n) \left( \frac{M - m}{\rho} \right) \nabla p \quad (23)$$

where the function  $g$  depends on the average momentum exchange in the collisions and can be evaluated only by considering the details of the collision dynamics.

For comparison, equation 12 leads to the following result for an inviscid binary mixture, disregarding thermal diffusion:

$$u_1 - u_2 = - \frac{n^2}{n_1 n_2} D_{12} \left[ \frac{1}{n} \nabla n_1 - \frac{n_1 n_2}{pn} \left( \frac{M - m}{\rho} \right) \nabla p - \frac{n_1 n_2 m_1 m_2}{p\rho} (F_1 - F_2) \right] \quad (24)$$

The mechanistic argument just given therefore leads to the correct phenomenological form for the pressure diffusion term, since the details of the collision dynamics are embodied in the binary diffusion coefficient in equation 24. This shows that pressure diffusion is a result of the body forces or inertial forces acting on the particles and arises because heavier particles must have a higher frequency of collisions if the collision force acting on them is to balance the greater body force and inertia force. As a consequence, the heavier particles must move faster relative to the mean flow, which leads to the difference in diffusion velocities expressed by equation 23. If the forces on the particle are initially unbalanced in the inertial coordinate system used in the discussion, the particle will accelerate until a steady state is reached in which there is

practically no acceleration relative to the mass-average flow. The assumption  $dV_1/dt \approx 0$ ,  $dV_2/dt \approx 0$  is therefore reasonable, and is in fact implicit in the definition of a steady-state diffusion velocity.

Since the effect of forces proportional to the mass is accounted for by pressure diffusion, the term in the diffusion equation due to external forces is identically zero if all acting external forces are proportional to mass, such as gravity or inertial forces. In that case the  $F_j$  and  $F_k$  of equation 11 can be replaced by  $\mathcal{F}$  for all  $j$  and  $k$ , and upon carrying out the summations indicated in equations 10 and 12, the external-force term vanishes. This is immediately obvious in the binary case, equation 24. This term will be important only if forces such as the coulomb interaction in an ionized gas are present. In that instance, for example, the total force acting on an electron and an ion due to the charge will be the same, but the force per unit mass will differ by a factor of  $\sim 1800$  or more.

The diffusion process in the atmosphere is a good example of pressure diffusion. The pressure diffusion due to gravity will cause both heavy and light constituents to drift downward, but the heavier particles will tend to sink with a greater velocity if this cause is considered alone, as has been explained. This effect must be counter-balanced by concentration diffusion, since there can be no net mass flow toward the earth. Thus, in a perfectly still atmosphere in equilibrium, all constituents will have larger concentrations near the earth, creating a concentration diffusion upward. The concentration gradients for the heavier components will be steeper to provide an upward concentration diffusion which will balance the corresponding pressure diffusion. Of course, this example is

greatly over-simplified, because in the real atmosphere effects due to turbulence will be present.

All the kinetic theory results needed for the analysis to follow, specifically the equations governing transport processes in gases, have been stated. However, before proceeding with that analysis, the other important means of studying transport phenomena, i. e. the thermodynamic theory of irreversible processes, or irreversible thermodynamics, will be considered briefly. It is hoped that this limited discussion will serve to contrast the kinetic theory and irreversible thermodynamics, and point out the relative advantages of each.

### The Thermodynamic Theory of Irreversible Processes

Many of the basic ideas underlying irreversible thermodynamics were either observed experimentally or accepted as intuitively reasonable a long time ago, but it is primarily in the last three decades that substantial progress has been made in unifying these ideas to form a macroscopic theory of irreversible processes. The impetus to the theory was provided by Onsager in 1931, when he showed that certain relationships exist between coefficients associated with the "fluxes" and "forces" which produce entropy in irreversible processes (15). Subsequent developments have been closely affiliated to the names of Onsager, Prigogine, Casimer, de Groot, Biot, and others. An exposition of the basic concepts of irreversible thermodynamics is given in a paper by Miller (16), and a comprehensive discussion is provided in the book by Prigogine (17). The subject is presented in greater detail in the book by de Groot (18), in which many applications are studied. The review given here will be based primarily on these three references.

Irreversible processes are usually associated with gradients or potentials in the system, such as a temperature gradient, pressure gradient, concentration gradient, chemical potential, electrical potential, etc. In irreversible thermodynamics these quantities are referred to as "forces", although usually they are not related to true forces in the Newtonian sense. The irreversible phenomena which arise due to these "forces", such as heat flow, diffusion flow, chemical reaction rate, electrical current, etc., are called "fluxes". It has long been well known that in a large class of problems involving irreversible processes, the "fluxes" and "forces" are related through simple, linear expressions. Familiar examples of these phenomenological laws are the Fourier law of heat conduction, Fick's law of diffusion, and Ohm's law. In a completely general case, where a number of irreversible processes are occurring simultaneously, any given "flux" might receive contributions from all of the "forces" present. It is therefore natural to try to generalize the simple phenomenological laws by writing them in the form:

$$J_i = \sum_{k=1}^n L_{ik} X_k \quad (25)$$

where the  $J_i$  and the  $X_k$  are the fluxes and forces, respectively, in the sense of irreversible thermodynamics. The  $L_{ik}$  are called the "phenomenological coefficients". For example, the diagonal members of this coefficient matrix, the  $L_{ii}$ , are the thermal conductivity, diffusion coefficient, electrical conductivity, etc.

The linear form of these generalized phenomenological laws cannot be theoretically justified, in general; instead, equation 25 is a postulated form which must rely on experimental verification. It is found that

the linear phenomenological laws adequately describe the irreversible processes in most situations of physical interest. The Onsager principle which led to the development of irreversible thermodynamics is concerned with the relationships among the phenomenological coefficients and applies only when the linear laws given by equation 25 are valid.

It is shown in irreversible thermodynamics that if the system is not too far from equilibrium the entropy production can always be expressed in terms of fluxes and forces in the following way:

$$\frac{ds_i}{dt} = \sum_{k=1}^n J_k X_k \quad . \quad (26)$$

The entropy production is defined as the rate at which entropy is produced within the system by irreversible processes. According to the second law of thermodynamics,

$$ds \geq \frac{dQ}{T}$$

where the equality applies to a reversible process, and  $dQ$  is the heat supplied to the system by the surroundings at the local temperature  $T$ . This can be restated as an equality,

$$\frac{ds}{dt} = \frac{1}{T} \frac{dQ}{dt} + \frac{ds_i}{dt} \quad (27)$$

and this expression may be regarded as a definition of the local entropy production.

The statement of equation 26 relies on the hypothesis that the state of a system sufficiently close to equilibrium can be described by the classical thermodynamic variables, such as internal energy, pressure, temperature, entropy, etc. This hypothesis has been accepted and used for a long time on an intuitive basis, being implied, of course, in Fourier's law,



Fick's law, and others, but in recent years it has been examined more carefully, notably by Prigogine (19). He has studied the hypothesis with respect to the specific case of transport processes in gases, using the Chapman-Enskog theory as a basis. Strictly speaking, the thermodynamic variables are defined only when the distribution function is given by  $f = f^{(0)}$  (the Maxwell-Boltzmann distribution). The use of thermodynamic variables outside equilibrium is conditioned by the proper convergence of the Enskog series:

$$f = f^{(0)} + \sigma f^{(1)} + \sigma^2 f^{(2)} + \dots$$

Taking this approach, Prigogine showed that for transport processes in gases the hypothesis upon which equation 26 is based, and therefore irreversible thermodynamics itself, is valid when the linear phenomenological laws, such as expressed by equation 25, are applicable.

The central feature of irreversible thermodynamics is the Onsager principle. This theorem states that if the proper choice of fluxes  $J_i$  and forces  $X_i$  is made, the matrix of phenomenological coefficients  $L_{ik}$  in equation 25 is symmetrical, i. e.:

$$L_{ik} = L_{ki} \quad (i, k = 1, 2, \dots, n) \quad (28)$$

These identities are known as the Onsager reciprocal relations. They express a connection between mutually-interfering, simultaneous, irreversible phenomena. One example is the effect of the temperature gradient on diffusion, i. e. thermal diffusion, and the analogous effect on the heat flux.

The "proper choice" of the fluxes and forces is made by calculating the entropy production for the process in question and expressing it in the form of equation 26. The proper choices are then defined by equation 26.

Some freedom in the choice usually exists, because ordinarily the terms of equation 26 can be split into several alternative sets of forces and fluxes. However, for any given choice the Onsager reciprocal relations will hold for the corresponding phenomenological coefficients.

The calculation of the entropy production, leading to an expression with the form of equation 26, is based on Gibbs' relation:

$$Tds = de + pd\left(\frac{1}{\rho}\right) - \sum_i \mu_i n_i \quad (29)$$

where  $e$  is the specific internal energy,  $p$  the pressure,  $\rho$  the density,  $\mu_i$  the chemical potential of species  $i$ , and  $n_i$  the concentration of  $i$ . This equation is thus used away from equilibrium and implies that the thermodynamic variables still are meaningful in the near-equilibrium state. This is how the hypothesis previously discussed in connection with equation 26 enters.

Before discussing diffusion and energy transport from the viewpoint of irreversible thermodynamics, the main features of the theory can now be summarized. The thermodynamic theory of irreversible processes utilizes the laws of classical thermodynamics, Newton's laws, and linear phenomenological laws describing irreversible processes, as well as a new hypothesis and a new law (Onsager's principle). The hypothesis states that near equilibrium the state of a system can be completely described by classical thermodynamic variables, and Onsager's principle provides symmetry relationships among the coefficients in the phenomenological laws. In practice, the theory consists of first finding the proper fluxes and forces from equation 26 by calculating the entropy production, and then studying the phenomenological equations in connection with the Onsager reciprocal relations. Like classical thermodynamics, it is en-

tirely a macroscopic theory, as opposed to the microscopic viewpoints of statistical mechanics and kinetic theory.

The application of irreversible thermodynamics to the problem of diffusion and energy transport in continuous media is considered in detail by de Groot (18) (Chapter VII), and only the basic features of that discussion will be presented here. Viscous effects will be neglected.

The equations needed to calculate the entropy production are the continuity equations for the individual species, 5, the equation of motion, 8 (where only the diagonal elements of the pressure tensor  $P$  are used, i. e. the static pressure  $p$ ), the energy equation, 9 (with the same comment regarding the pressure), and Gibbs' equation, 29. In accepting the Gibbs' relation it is implied that the entropy depends explicitly on the internal energy, density, and concentrations, and only implicitly on the space and time coordinates. This equation is therefore supposed to be correct when the differentials are convective derivatives, defined by:

$$\frac{d}{dt} = \frac{\partial}{\partial t} + (V_o \cdot \nabla) \quad . \quad (30)$$

By taking the convective derivative of the Gibbs' equation and introducing equations 5, 8 and 9, the entropy production can be evaluated.

The result is:

$$\rho \frac{ds}{dt} = - \nabla \cdot \left( \frac{J_q - \sum \mu_k J_k}{T} \right) + \frac{J_q \cdot X_q + \sum J_k \cdot X_k + A J_c}{T} \quad . \quad (31)$$

This is a continuity equation for entropy. It states that the local change in specific entropy is due to the negative divergence of an entropy flux plus the entropy production (divided by temperature). The latter has already been written in terms of "fluxes" and "forces", which are defined by:

$$J_q = Q \text{ (heat flux)}$$

$$X_q = - \nabla T / T$$

$$J_k = \rho_k u_k = m_k n_k u_k = \text{diffusion flux}$$

$$X_k = F_k - T \nabla (\mu_k / T) = \text{diffusion force}$$

$$J_c = m_k K_k = \text{mass rate of production of species } k$$

$$A = - \sum \mu_k \nu_k, \text{ called the chemical affinity, where } \nu_k \text{ are the stoichiometric numbers.}$$

The corresponding phenomenological equations are:

$$J_i = \sum_{k=1}^n L_{ik} X_k + L_{iq} X_q$$

$$J_q = \sum_{k=1}^n L_{qk} X_k + L_{qq} X_q \quad (32)$$

$$J_c = L A$$

The chemical reaction rate has been written as independent of the forces  $X_q$  and  $X_k$ . This is because  $J_c$  and  $A$  are scalars, while the remaining forces and fluxes are vectors, and the tensorial character must be uniform in the equations. As a consequence of the definition of the diffusion velocity, equation 4,  $\sum_k J_k = 0$ ; this leads to auxiliary conditions on the coefficients

$$\sum_{k=1}^n L_{ik} = 0 \quad (i = 1, 2, \dots, n)$$

$$\sum_{i=1}^n L_{ik} = 0 \quad (k = 1, 2, \dots, n)$$

These are not all independent, of course.

As a specific example, consider the binary case. The formalism just described then leads to:

$$J_1 = -J_2 = -L_{11} \left[ \left( \frac{\partial \mu_1}{\partial n_1} \right)_{T,p} \frac{1}{n_2} \nabla n_1 - (v_1 - v_2) \nabla p + F_1 - F_2 \right] - \left[ L_{q1} - L_{11}(h_1 - h_2) \right] \frac{\nabla T}{T} \quad (33)$$

$$J_q = -L_{q1} \left[ \left( \frac{\partial \mu_1}{\partial n_1} \right)_{T,p} \frac{1}{n_2} \nabla n_1 - (v_1 - v_2) \nabla p + F_1 - F_2 \right] - \left[ L_{qq} - L_{q1}(h_1 - h_2) \right] \frac{\nabla T}{T} \quad (34)$$

In obtaining these results, it was noted that the chemical potential  $\mu_k$  is a function of temperature, pressure, and concentrations, so that:

$$\nabla \mu_k = -s_k \nabla T + v_k \nabla p + \sum_{i=1}^{n-1} \frac{\partial \mu_k}{\partial n_i} \nabla n_i \quad (35)$$

where  $s_k$  and  $v_k$  are the partial specific entropy and volume of species  $k$ , respectively. The partial specific enthalpy  $h_k = \mu_k + Ts_k$ . The Gibbs-Duhem relation,  $n_1 d\mu_1 + n_2 d\mu_2 = 0$  at constant  $T$  and  $p$ , was also used.

The appearance of the same coefficient,  $L_{q1}$ , in the last term of the diffusion flux equation (thermal diffusion) and the first term of the heat flux equation is a result of the Onsager reciprocal relation  $L_{1q} = L_{q1}$ . Thermal diffusion and the corresponding effect on the energy flux are "mutual interference" effects, which accounts for this reciprocity.

By comparing equations 33 and 34 with the equivalent kinetic theory results, equations 10 and 14, it can be seen that irreversible thermodynamics leads to the correct phenomenological form for the diffusion flux and heat flux. In a relatively simple way, this macroscopic theory shows that in the absence of a temperature gradient and external forces not proportional to mass, the proper "driving force" for diffusion is the chemical potential, not the concentration gradient alone, as in Fick's law. Pressure diffusion is therefore included in the formalism.

At first it might seem desirable to utilize this information in the mathematical formulation of diffusion problems, replacing the concentration diffusion and pressure diffusion by a single term which is proportional to the gradient of the chemical potential. A solution conforming to a single set of boundary conditions on the chemical potential would correspond to a continuous array of different boundary conditions on the pressure and concentration. This would show the change in concentration boundary conditions required to maintain a constant total diffusion strength when there is a given adjustment in the pressure boundary conditions, for example. In a sense, the relative strengths of pressure diffusion and concentration diffusion might be demonstrated in this way.

However, for a number of reasons this approach is unattractive and impractical. The foremost argument against such a procedure is the fact that a clear physical explanation can be ascribed to the individual mechanisms of concentration diffusion and pressure diffusion. In contrast, the chemical potential is a more-or-less formal device which is not directly measurable. The quantities which can be easily measured and controlled at the boundaries are the pressure and temperature, and it

is therefore desirable to express the boundary conditions directly in terms of these variables. Also, introducing the chemical potential into the formalism will not simplify the problem by eliminating a variable, such as the pressure, because pressure diffusion is not the only mechanism through which the pressure gradient can influence the solution when chemical reactions are present, as will be shown.

Unlike kinetic theory, irreversible thermodynamics cannot provide detailed information about the phenomenological coefficients. For this reason, the kinetic theory is the more satisfactory approach in most cases concerned with transport properties in gases, since it yields everything given by irreversible thermodynamics as well as numerical values for the coefficients, although at the expense of much greater complexity. The chief merit of irreversible thermodynamics is that it provides a simple means of correlating the various irreversible phenomena present and showing how they are interrelated. However, microscopic theories based on the transport equations for the particles, such as the kinetic theory of gases, are available for only special kinds of irreversible phenomena, and are based on an idealized model. On the other hand, irreversible thermodynamics is a general macroscopic theory for irreversible processes, capable of treating problems such as viscoelastic phenomena in solids, for example. Therefore, the importance of this theory is much greater than it might seem to be from the example given here.

In this section the fundamental features of the theories of transport processes in gases have been surveyed, and the pertinent equations stemming from these theories have been summarized. In subsequent sections these equations will be treated as phenomenological relations

describing the transport phenomena, and the details of the underlying theory will not be considered further. Taking this approach, the effects of diffusion on heat transfer in a reacting gas mixture will be studied, and in particular, the effect of a pressure gradient in the gas will be investigated. Thermal diffusion and the related energy flux phenomenon given by the last term in equation 14 are usually relatively small effects and will be neglected here.



### III. THE BINARY DISSOCIATING GAS IN THE CHANNEL-FLOW APPROXIMATION

As the transport equations of the previous section show, pressure diffusion may either promote or impede energy transport, depending on whether the pressure gradient is aligned with the temperature gradient, or against it. If the mixture is undergoing chemical reactions, the presence of a pressure gradient can affect energy transport in another, somewhat less direct, way. The reaction rate at any point in the flow depends on the frequency of collisions between molecules of the reacting species, and therefore on the local density. By influencing the density distribution in the reacting gas, the pressure gradient therefore changes the concentration distributions of the various species, and so the concentration gradients. Thus the energy transport is indirectly affected by the pressure gradient through the mechanism of concentration diffusion. Furthermore, the reactions act as heat sources or sinks distributed throughout the flow, due to the heat of reaction expelled or absorbed, and the pressure gradient changes this distribution by means of the effect of density on the reaction rates. This also influences energy transfer to some extent.

Of course, the last two effects mentioned are, strictly speaking, influences of the local pressure (not the local pressure gradient) on the density, and indirectly on the energy transport. However, the local pressure is determined by specifying the pressure at an arbitrary point together with the value of some parameter which characterizes the pressure gradient, and changes which depend on the value of that parameter are termed "pressure gradient effects" here. As examples of such a

parameter, the pressure gradient in the atmosphere would be characterized by the gravitational constant, and in a vortex flow by the Mach number.

As previously mentioned, a situation of considerable practical interest in which pressure gradient effects may play a role occurs when a reacting gas mixture rotates about an axis, as in a vortex or a solid-body rotation. The radial acceleration of the fluid creates a pressure gradient normal to the streamlines, and under some circumstances, this may strongly influence radial heat transfer. Flows of this kind might therefore serve well as a framework for the study of energy transport in reacting gases in general, and pressure gradient effects in particular. The simplest example is a vortex or a solid-body rotation of a pure, diatomic, dissociating gas, but even this is a formidable problem, involving the solution of coupled, non-linear differential equations. The difficulty is compounded by the many geometric factors introduced into the equations by the cylindrically-symmetric nature of the problem.

To reduce the complications associated with this problem so that analytic solutions are practical, while still retaining the interesting features, a limiting case will be used as the model for the present work. The flow of a pure two-component dissociating gas is assumed to be confined between two concentric, infinitely long cylinders, which rotate with the flow. The radius of the inside cylinder  $r_0$  is much greater than the difference in radii of the cylinders,  $w$ . Therefore, curvature effects can be neglected and the flow treated as if it were in a channel of width  $w$ . The hot wall is taken to be at the inside cylinder ( $r = r_0$ ), and the temperature and pressure there are  $T_0$  and  $p_0$ , respectively. A pressure gradient normal to the walls can be induced by a high rotational velocity

of the cylinders.

The dissociation reaction can be represented by the symbolical equation:



where  $A_2$  and  $A_1$  represent the chemical symbols of the molecular and atomic species, respectively, and  $k_f$  and  $k_b$  are the forward and backward rate constants. The steady-state equations appropriate to this reaction and the model just described can be obtained from the general equations given in the preceding section. Here, they will be written in terms of dimensionless variables.

If the gas obeys the perfect gas law,  $p = n\mathcal{R}T$ , the radial equation of motion, given by equation 8, can be written

$$\frac{d \ln \pi}{d\eta} = \frac{2\beta}{\theta} \left( \frac{V}{V_{(\eta=0)}} \right)^2$$

where  $\pi = p/p_0$ ,  $\theta = T/T_0$ ,  $V$  = tangential velocity, and  $\eta = r - r_0/w$ . The parameter  $\beta$  characterizes the pressure gradient, and within the framework of the present model,

$$\beta = \frac{w\gamma M^2}{2 r_0} \quad (37)$$

where  $M$  is the Mach number at the hot wall ( $\eta = 0$ ), and  $\gamma$  is a mean specific heat ratio,  $\gamma = \overline{C_p}/\overline{C_v}$ . In the channel-flow approximation, the tangential velocity appears only in the equation of motion and can therefore be specified with some freedom. Recognizing this, it is consistent with the geometry approximation to rewrite the equation of motion:

$$\frac{d \ln \pi}{d \eta} = \frac{2\beta}{1 - E^{(o)} \eta} \quad (38)$$

where  $T(\eta = 1)/T_o = 1 - E^{(o)}$ . This form of the equation will be used in the work to follow.

According to the definition of the diffusion velocity, given by equation 4:

$$n_1 m_1 u_1 + n_2 m_2 u_2 = 0 \quad (39)$$

or, since  $m_2/m_1 = 2$  :

$$u_2 = - \frac{x}{2(1-x)} u_1 \quad (40)$$

where  $x$  is the mole fraction of the atomic species, defined by  $x = n_1/n$ , and  $n_2$  has been eliminated by noting that  $n_1 + n_2 = n$ .

The energy equation is obtained from equation 9. Since the tangential mass-average velocity vanishes (no radial mass flow), this equation can be integrated at once to obtain  $Q = \text{constant}$ . The energy flux  $Q$  is given by equation 14; ignoring the last term (which is relatively small) and eliminating  $u_2$  with equation 40:

$$- \frac{d\theta}{d\eta} + H\Gamma = \frac{wQ}{\lambda T_o} = E \quad (41)$$

where

$$\theta = T/T_o$$

$$\Gamma = n_1 u_1 / n D_{12} \quad (n D_{12} \approx \text{constant})$$

$$H = Le(h_1 - \frac{m_1}{m_2} h_2) / \bar{C}_p T_o \approx Le(\Delta H_{f1} - \frac{1}{2} \Delta H_{f2}) / \bar{C}_p T_o$$

$$E = \text{total dimensionless energy transport} = \text{constant.}$$

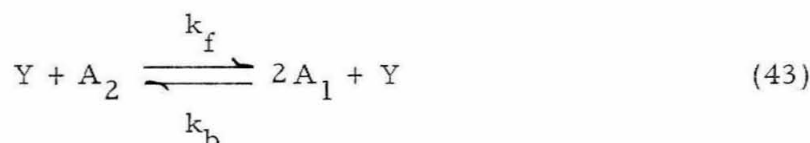
In this expression the small temperature dependence of  $n D_{12}$ ,  $\lambda$ , and  $\bar{C}_p$  have been ignored. The quantity  $\Gamma$  is the dimensionless diffusion

flux of the atomic species;  $H$  will be regarded as a constant here, given by the approximate expression, where  $\Delta H_{fi}$  is the heat of formation of species  $i$ , and  $Le$  is the Lewis number, defined by  $Le = \overline{C}_p n D_{12} / \lambda$ . The approximation regarding the enthalpy-difference bracket is exactly true if  $C_{p1} = \frac{1}{2} C_{p2}$ , and is usually quite reasonable in view of the relatively large values of the heats of formation. The first term of equation 41 represents the energy transport due to ordinary conduction, and the second represents the energy carried by diffusion.

The diffusion equation follows from equations 11 and 12. Thermal diffusion, given by the last term in 12, is disregarded in the present work. In terms of the dimensionless variables chosen here, the result is:

$$\Gamma = - \left( \frac{2x}{2-x} \right) \frac{d \ln x}{d\eta} - \frac{2x(1-x)}{(2-x)^2} \frac{d \ln \pi}{d\eta} . \quad (42)$$

The remaining equation needed to describe the problem is the continuity equation for one of the reacting species, say, the atomic species. This is obtained from equations 5 and 16. The dissociation of the pure gas will be assumed to proceed according to the reaction



where  $Y$  represents the third particle needed for the three-body recombination reaction; this can be either an atom  $A_1$  or a molecule  $A_2$ . Therefore, in equation 16 the concentration corresponding to  $Y$  is that of the total mixture,  $n$ .

The recombination rate constant  $k_b$  is given by the Arrhenius law (20) (pp. 57-61):

$$k_b = Z e^{-E_A/kT} \quad (44)$$

where  $E_A$  is the activation energy,  $k$  is Boltzmann's constant, and  $Z$  is usually called the "frequency factor". This equation can be crudely interpreted as the total number of collisions between molecules or atoms entering into the reaction, represented by  $Z$ , multiplied by the fraction of those collisions resulting in a chemical reaction. The activation energy for atom recombination is found to be either zero or very small, and in the present work it will be neglected, i. e.,  $E_A = 0$ .

It has already been assumed in connection with equation 37 that the mixture is a perfect gas, i. e.:

$$p = n R T \quad (45)$$

The continuity equation for the atomic species can then be written:

$$\frac{d\Gamma}{d\eta} = 2R \left[ \frac{K_n}{n_o} (1-x) - x^2 \frac{\pi}{\theta} \right] \pi^2 \theta^{m-2} \quad (46)$$

where  $K_n$  is the concentration equilibrium constant, i. e.,

$$K_n = (n_1^2/n_2)_{\text{equil.}} = k_f/k_b,$$

$n_o$  is the total concentration at the hot wall, and  $R$ , a dimensionless constant, is a rate parameter defined by:

$$R = \left( \frac{w^2 k_b n^3}{n D_{12}} \right)_{\eta=0} \quad (47)$$

Since  $R$  is evaluated at the hot wall, the factor  $\pi^2 \theta^{m-2}$  is required to account for the variation of  $n$ ,  $k_b$ , and  $D_{12}$  with pressure and temperature. According to the first-approximation kinetic theory calculation based on the billiard-ball model, the product  $n D_{12}$  is proportional to  $T^{\frac{1}{2}}$  and independent of pressure. If the activation energy is

zero,  $k_b = Z$ , and the frequency factor  $Z$  is generally independent of pressure but proportional to some moderate power of the temperature. Therefore,  $k_b/nD_{12}$  can be represented as proportional to  $T^m$ .

The magnitude of the rate parameter  $R$  determines the chemical state of the dissociating gas. It is essentially the ratio of recombination reaction rate to diffusion rate. To be more precise,  $R$  has the order-of-magnitude of a characteristic diffusion time for the length  $w$  divided by a characteristic reaction time. For example, if  $R \gg 1$ , compensation for any temporary local departure from chemical equilibrium resulting in a local excess of atoms will be accomplished by recombination very quickly relative to the time required for diffusion to remove the excess atoms from the region. As a result, the gas composition will be very nearly in chemical equilibrium at the local temperature. Conversely, if  $R \ll 1$ , the flow will be nearly chemically "frozen".

Equations 37, 41, 42 and 46 are sufficient to completely describe the flow in terms of the dependent variables  $\theta$ ,  $\pi$ ,  $\Gamma$ , and  $x$ . Although a considerable simplification has been introduced by the channel-flow approximation, nothing has been done to eliminate the coupled, non-linear character of the system of equations. To alleviate these difficulties and make analytic solutions feasible, additional restrictions must be imposed on the problem. These consist primarily of (a) considering only small degrees of dissociation, i.e.,  $x \ll 1$ , and (b) considering only near-frozen ( $R \ll 1$ ) or near-equilibrium ( $R \gg 1$ ) flow. With these two restrictions, a perturbation technique can be used to investigate limiting cases of particular interest, corresponding to different boundary conditions and different chemical regimes. The details of the perturbation treatment are developed in subsequent sections, where the various cases

are considered separately.



#### IV. CHEMICALLY FROZEN AND NEAR-FROZEN FLOW OF THE BINARY GAS

In this section the channel-flow approximation is used to study transport phenomena in a chemically frozen, or nearly frozen, pure, dissociating, diatomic gas. This chemical state prevails when the reaction rate is low relative to the diffusion rate for the characteristic length  $w$ . In general, under these circumstances the rate parameter  $R \ll 1$ , as explained in the preceding section. This provides the basis for a perturbation solution expressed as a series in a small parameter  $\delta$  proportional to  $R$ . The appropriate parameter  $\delta$  is not necessarily equal to  $R$ , however, because the chemical state also depends on the local extent of dissociation, which is not accounted for by  $R$ . For example, if the gas is at a relatively low temperature and only slightly dissociated, even a large change in  $R$  which tends to enhance recombination cannot alter the chemical state radically, because extensive recombination clearly requires the presence of a high proportion of atoms. Conversely, at high temperatures a small adjustment in  $R$  may affect the chemical state appreciably. The definition of  $\delta$  should therefore recognize that the chemical reaction rate depends on the concentrations of the species involved as well as the rate constant and other factors.

The analysis is also confined to low degrees of dissociation. This restriction is introduced into the formalism through a second small, dimensionless number  $\epsilon$ , and the solution is expressed as a two-parameter expansion in  $\epsilon$  and  $\delta$ . The extent of dissociation can be controlled indirectly by limiting the pressure and temperature range of the gas, through the boundary conditions. The mole fraction of the atoms is re-

lated to the equilibrium constant  $K_n$ , which in turn depends on the temperature. When the gas is in local chemical equilibrium, the mole fraction  $x$  is determined at each point in the mixture by the local value of  $K_n$ , since in equilibrium  $K_n/n = x^2/(1-x)$ , where  $n$  is the molar concentration of the mixture. On the other hand, when the gas is chemically frozen, the mole fraction tends to assume a value somewhere between the large and small extremes which correspond to chemical equilibrium at the temperatures of the hot and cold walls, respectively. Therefore, the extent of dissociation can always be restricted by putting suitable bounds on the equilibrium constant, or really on the ratio  $K_n/n$ , through the temperature and pressure boundary conditions. It follows that the parameter  $\epsilon$  can be defined in terms of the equilibrium constant. The specific definitions of  $\epsilon$  and  $\delta$  will be given presently.

The dependent variables, as well as the eigenvalue  $E$  of equation 41, are expressed according to the following expansions:

$$\begin{aligned}\theta &= \theta^{(0)} + \epsilon(\theta^{(10)} + \delta \theta^{(11)} + \dots) + O(\epsilon^2) + O(\delta^2) \\ x &= 0 + \epsilon(x^{(10)} + \delta x^{(11)} + \dots) + O(\epsilon^2) + O(\delta^2) \\ \Gamma &= 0 + \epsilon(\Gamma^{(10)} + \delta \Gamma^{(11)} + \dots) + O(\epsilon^2) + O(\delta^2) \\ E &= E^{(0)} + \epsilon(E^{(10)} + \delta E^{(11)} + \dots) + O(\epsilon^2) + O(\delta^2)\end{aligned}\tag{48}$$

The eigenvalue  $E$  corresponds physically to the total energy transport; therefore it has to be expressed in the same form as the dependent variables, because perturbations in the temperature profile or diffusion flux lead to changes in the energy transport.

When  $\epsilon = 0$  there is no dissociation. Thus, the zeroth-order solution corresponds to a simple gas composed entirely of the molecular species, and the  $O(\epsilon)$  solution gives the leading effect of dissociation.

When  $\delta = 0$  the mixture is chemically frozen, i.e. there are no chemical reactions occurring. The leading effect of a departure from the completely frozen state is given by the  $O(\epsilon\delta)$  solution. There are no terms  $O(\delta)$ , which reflects the dependence of rate effects on the degree of dissociation present.

Only the terms which contain the leading influence of dissociation and rate effects are retained in the present work. For example, the  $O(\epsilon^2)$  solution gives the second-order influence of dissociation. Since this is essentially a correction to the first approximation given by the  $O(\epsilon)$  terms and provides qualitative information of secondary importance, it is discarded.

When these expansions are substituted into equations 41, 42 and 46, and coefficients of equal powers of  $\epsilon$  and  $\delta$  are equated, a set of linear differential equations for each of the groups of unknown functions of a given order in  $\epsilon$  and  $\delta$  (e.g.  $\theta^{(10)}$ ,  $x^{(10)}$ , and  $\Gamma^{(10)}$ ) is obtained. The zeroth-order solution is particularly simple, because it corresponds to a single, non-reacting gas transporting energy by heat conduction alone. It is given by the energy equation

$$-\frac{d\theta^{(0)}}{d\eta} = E^{(0)} = \frac{wQ}{\lambda T_0} \quad (49)$$

from which:

$$\theta^{(0)} = 1 - E^{(0)}\eta \quad (50)$$

The eigenvalue  $E^{(0)}$  is the zeroth-order dimensionless heat transfer and is determined by specifying the temperature ratio  $\theta = T/T_0$  at the cold wall ( $\eta = 1$ ).

The form of the equation of motion to be used in the channel-flow

approximation was given by equation 38. According to equation 50, this can be written:

$$\frac{d \ln \pi}{d \eta} = \frac{2\beta}{1 - E^{(0)}\eta} = \frac{2\beta}{\theta^{(0)}} \quad (51)$$

Integration of this equation gives the pressure distribution in the channel:

$$\pi = (1 - E^{(0)}\eta)^{-2\beta/E^{(0)}} \quad (52)$$

Before proceeding with the solution, the dimensionless expansion parameters  $\epsilon$  and  $\delta$  can now be defined more specifically. The small number  $\epsilon$  is defined by restricting the magnitude of the equilibrium constant. Using the temperature expansion given by equation 48 and noting that  $K_n/n_o$  can be closely approximated by an exponential function of temperature:

$$\begin{aligned} \frac{K_n}{n_o} = C e^{-\theta_a/\theta} \approx C e^{-\theta_a/\theta^{(0)}} & \left[ 1 + \epsilon \frac{\theta_a \theta^{(10)}}{(\theta^{(0)})^2} \right. \\ & \left. + \epsilon \delta \frac{\theta_a \theta^{(11)}}{(\theta^{(0)})^2} + \dots \right] \end{aligned}$$

where  $K T_o \theta_a = E_A$ , the activation energy for dissociation, and  $C$  is a dimensionless constant. Since the hot wall must be at a relatively high temperature to provide appreciable dissociation in the gas, practically all problems of interest will be such that the temperature difference between the walls is much less than the temperature of the hot wall, or  $E^{(0)} \ll 1$ . Therefore:

$$C e^{-\theta_a/\theta^{(0)}} = C e^{-\theta_a/(1-E^{(0)}\eta)} \approx C e^{-\theta_a} e^{-\theta_a E^{(0)}\eta}.$$

Let:

$$\epsilon = (C e^{-\theta_a})^{\frac{1}{2}} = \left[ \frac{K_n(\eta = 0)}{n_o} \right]^{\frac{1}{2}} \ll 1 \quad (53)$$

$$\alpha = \theta_a E^{(0)} \quad (54)$$

Then in equation 46:

$$\frac{K_n}{n_o} = \epsilon^2 e^{-\alpha\eta} \left[ 1 + \epsilon \frac{\theta_a \theta^{(0)}}{(\theta^{(0)})^2} + \epsilon \delta \frac{\theta_a \theta^{(11)}}{(\theta^{(0)})^2} + \dots \right] \quad (55)$$

As discussed previously, this definition of  $\epsilon$  is clearly related to the degree of dissociation, since when the gas is in local equilibrium,  $K_n = n_1^2/n_2$ . In fact, when  $\epsilon \ll 1$ , it is approximately equal to the equilibrium mole fraction  $x_e$  at the temperature of the hot wall. This can be seen by substituting equations 48 and 55 into 46 and letting  $R \rightarrow \infty$  (which corresponds to chemical equilibrium), so that at the hot wall,  $x^2 = (1-x)K_n/n_o$ . Since the perturbation analysis requires that  $\epsilon \ll 1$ , there is an effective upper limit on the hot-wall temperature  $T_o$  which can be considered. The range within which  $T_o$  must fall depends on the particular gas under study, of course.

The remaining expansion parameter  $\delta$  is defined by the relation:

$$\delta = \epsilon R \ll 1. \quad (56)$$

This definition recognizes that rate effects are not independent of the degree of dissociation. If there is very little dissociation, even large changes in the rate parameter  $R$  will be of little consequence in altering the chemical state, and the magnitude of  $\delta$  will be almost unchanged; when dissociation is extensive, a small change in  $R$  may have a large influence on the chemical state.

As already mentioned, the solution will be carried to  $O(\epsilon\delta)$ ,

which will show the first-order effect of dissociation ( $\epsilon$ ) and the first-order effect of rates ( $\epsilon\delta$ ). The equations pertinent to near-frozen flow are obtained by substituting equation 48 into 41, 42, and 46, and combining the results with equation 51. The zeroth-order energy equation and solution have already been given by 49 and 50. The higher-order equations are:

$$-\frac{d\theta^{(1j)}}{d\eta} + H\Gamma^{(1j)} = E^{(1j)} \quad j = 0, 1 \quad (57)$$

where the eigenvalues  $E^{(1j)}$  are perturbations on the energy transport due to dissociation and rate effects.

After eliminating the pressure gradient with equation 51, the diffusion equation leads to:

$$\Gamma^{(1j)} = -\frac{dx^{(1j)}}{d\eta} - \frac{\beta x^{(1j)}}{1-E^{(0)}\eta} \quad j = 0, 1 \quad (58)$$

From the continuity equation:

$$\frac{d\Gamma^{(10)}}{d\eta} = 0, \text{ or } \Gamma^{(10)} = \text{constant} \quad (59)$$

and

$$\frac{d\Gamma^{(11)}}{d\eta} = 2 \left[ e^{-\alpha\eta} - (x^{(10)})^2 (1-E^{(0)}\eta)^{-(1+2\beta/E^{(0)})} \right] \cdot (1-E^{(0)}\eta)^{m-2} - 4\beta/E^{(0)} \quad (60)$$

Solutions to these equations will be obtained for two kinds of boundary conditions, representing limiting cases. In the first case, the walls are assumed to be perfectly catalytic, enhancing the reaction so that at each wall the composition is forced into local chemical equilibrium at the surface temperature. In the other case, the walls are non-catalytic

and no reactions take place at the surface. Therefore, every particle which strikes the wall is repelled unchanged, and the diffusion velocity vanishes at the surface.

### Perfectly Catalytic Walls

With the aid of equation 59, the  $O(\epsilon)$  diffusion equation given by 58 can be integrated at once to give the concentration distribution:

$$x^{(10)} = \frac{\Gamma^{(10)}(1-E^{(0)}\eta)}{E^{(0)}-\beta} + F^{(10)}(1-E^{(0)}\eta)^{\beta/E^{(0)}} \quad (61)$$

where  $F^{(10)}$  is the integration constant. The  $O(\epsilon)$  diffusion flux  $\Gamma^{(10)}$  is determined by the catalytic wall boundary conditions on the concentration. When the gas is in chemical equilibrium, the composition is determined by the equilibrium constant (see equation 46):

$$\frac{x_e^2}{1-x_e} = \frac{K_n}{n_o} \frac{\theta}{\pi} \quad (62)$$

When equations 48 and 55 are substituted into 62, the boundary conditions on  $x^{(10)}$  for catalytic walls can be obtained by equating terms  $O(\epsilon)$ .

Thus:

$$\begin{aligned} x^{(10)}(0) &= 1 \\ x^{(10)}(1) &= e^{-\alpha/2(1-E^{(0)})^{\frac{1}{2}} + \beta/E^{(0)}} \end{aligned} \quad (63)$$

Therefore, from equation 61:

$$\begin{aligned} \Gamma^{(10)} &= \frac{(E^{(0)}-\beta) [1 - e^{-\alpha/2(1-E^{(0)})^{\frac{1}{2}}}] }{1 - (1-E^{(0)})^{1 - \beta/E^{(0)}}} \\ F^{(10)} &= 1 - \frac{\Gamma^{(10)}}{E^{(0)} - \beta} \end{aligned} \quad (64)$$

Since  $\Gamma^{(10)} = \text{constant}$ , the energy equation, given by 57, yields:

$$\theta^{(10)} = (H\Gamma^{(10)} - E^{(10)})\eta + G^{(10)} .$$

The boundary conditions on the temperature are exactly satisfied by equation 50. Therefore,  $\theta^{(10)}(0) = \theta^{(10)}(1) = 0$ , which means that  $G^{(10)} = 0$ ,  $E^{(10)} = H\Gamma^{(10)}$ , and  $\theta^{(10)} = 0$ , everywhere. In particular, the perturbation on the heat transfer due to dissociation is a result of energy transport by diffusion and is given by:

$$E^{(10)} = H\Gamma^{(10)} = \frac{H(E^{(0)} - \beta) [1 - e^{-\alpha/2(1-E^{(0)})^{1/2}}]}{1 - (1-E^{(0)})^{1-\beta/E^{(0)}}} \quad (65)$$

This result is valid for a completely frozen flow where  $\delta = 0$ , such as a mixture of two inert gases with the molecular weight ratio  $m_2/m_1 = 2$ . To determine the first-order effect of non-zero rates, consider equation 60. Making use of equation 61, it becomes:

$$\begin{aligned} \frac{d\Gamma^{(11)}}{d\eta} = & 2e^{-\alpha\eta} (1-E^{(0)})\eta^{m-2} - 4\beta/E^{(0)} - 2C_1 (1-E^{(0)})\eta^{m-1} - 6\beta/E^{(0)} \\ & - 4C_2 (1-E^{(0)})\eta^{m-2} - 5\beta/E^{(0)} - 2(F^{(10)})^2 (1-E^{(0)})\eta^{m-3} - 4\beta/E^{(0)} \end{aligned}$$

where

$$C_1 = \left( \frac{\Gamma^{(10)2}}{E^{(0)} - \beta} \right), \quad C_2 = \left( \frac{\Gamma^{(10)}F^{(10)}}{E^{(0)} - \beta} \right),$$

$$\text{and } \alpha = \theta_a E^{(0)} .$$

For most cases of interest,  $\alpha$  is in the range  $4 \lesssim \alpha \lesssim 10$ . Therefore the term containing  $e^{-\alpha\eta}$  can be integrated by parts, and it is reasonable to neglect terms of order  $1/\alpha^3$ . Thus:



$$\begin{aligned}
 \Gamma^{(11)} = & -\frac{2e^{-\alpha\eta}}{\alpha} (1-E^{(o)}\eta)^{m-2-4\beta/E^{(o)}} + \frac{2E^{(o)}}{\alpha^2} (m-2-\frac{4\beta}{E^{(o)}}) \cdot \\
 & \cdot (1-E^{(o)}\eta)^{m-3-4\beta/E^{(o)}} + \frac{2C_1}{E^{(o)}} \frac{(1-E^{(o)}\eta)^{m-6\beta/E^{(o)}}}{(m-6\beta/E^{(o)})} \\
 & + \frac{4C_2(1-E^{(o)}\eta)^{m-1-5\beta/E^{(o)}}}{E^{(o)}(m-1-5\beta/E^{(o)})} \\
 & + \frac{2(F^{(10)})^2(1-E^{(o)}\eta)^{m-2-4\beta/E^{(o)}}}{E^{(o)}(m-2-4\beta/E^{(o)})} + F^{(11)}
 \end{aligned} \tag{66}$$

where  $F^{(11)}$  is an integration constant.

The rate effect on the concentration distribution is determined by the diffusion equation,

$$\frac{dx^{(11)}}{d\eta} + \frac{\beta x^{(11)}}{1-E^{(o)}\eta} = -\Gamma^{(11)}$$

where  $\Gamma^{(11)}$  is given by equation 66. Integration yields:

$$\begin{aligned}
 x^{(11)} = & -\frac{2}{\alpha^2} e^{-\alpha\eta} (1-E^{(o)}\eta)^{m-2-4\beta/E^{(o)}} + \frac{2C_1(1-E^{(o)}\eta)^{m+1-6\beta/E^{(o)}}}{(E^{(o)})^2(m-6\beta/E^{(o)})(m+1-7\beta/E^{(o)})} \\
 & + \frac{4C_2(1-E^{(o)}\eta)^{m-5\beta/E^{(o)}}}{(E^{(o)})^2(m-6\beta/E^{(o)})(m-1-5\beta/E^{(o)})} + 2\frac{(F^{(10)})^2}{E^{(o)}} \\
 & \cdot \frac{(1-E^{(o)}\eta)^{m-1-4\beta/E^{(o)}}}{(m-2-4\beta/E^{(o)})(m-1-5\beta/E^{(o)})} + \frac{F^{(11)}(1-E^{(o)}\eta)}{E^{(o)}(1-\beta/E^{(o)})} + D^{(11)}(1-E^{(o)}\eta)^{\beta/E^{(o)}}
 \end{aligned} \tag{67}$$

The appropriate boundary conditions are obtained as before from equation 62. This gives:

$$x^{(11)}_{(0)} = x^{(11)}_{(1)} = 0 .$$

Application of these boundary conditions determines the constants  $D^{(11)}$  and  $F^{(11)}$ .

$$\begin{aligned} D^{(11)} &= \frac{2}{\alpha^2} - \frac{2 C_1}{(E^{(o)})^2 (m-6\beta/E^{(o)}) (m+1-7\beta/E^{(o)})} \\ &\quad - \frac{4 C_2}{(E^{(o)})^2 (m-6\beta/E^{(o)}) (m-1-5\beta/E^{(o)})} \\ &\quad - 2 \left( \frac{F^{(10)}}{E^{(o)}} \right)^2 \frac{1}{(m-2-4\beta/E^{(o)}) (m-1-5\beta/E^{(o)})} - \frac{F^{(11)}}{E^{(o)} (1-\beta/E^{(o)})} \\ F^{(11)} &= \frac{E^{(o)} (1-\beta/E^{(o)})}{1-(1-E^{(o)})^{1-\beta/E^{(o)}}} \left\{ \frac{2}{\alpha} \left[ 1 - e^{-\alpha (1-E^{(o)})^{m-2-5\beta/E^{(o)}}} \right] \right. \\ &\quad - \frac{2C_1 \left[ 1 - (1-E^{(o)})^{m+1-7\beta/E^{(o)}} \right]}{(E^{(o)})^2 (m-6\beta/E^{(o)}) (m+1-7\beta/E^{(o)})} - \frac{4C_2 \left[ 1 - (1-E^{(o)})^{m-6\beta/E^{(o)}} \right]}{(E^{(o)})^2 (m-6\beta/E^{(o)}) (m-1-5\beta/E^{(o)})} \\ &\quad \left. - 2 \left( \frac{F^{(10)}}{E^{(o)}} \right)^2 \frac{\left[ 1 - (1-E^{(o)})^{m-1-5\beta/E^{(o)}} \right]}{(m-2-4\beta/E^{(o)}) (m-1-5\beta/E^{(o)})} \right\} \end{aligned} \quad (68)$$

With  $F^{(11)}$  given by 68, equation 66 can be substituted into the energy equation, given by

$$- \frac{d\theta^{(11)}}{d\eta} + H \Gamma^{(11)} = E^{(11)}$$

and integration yields:

$$\begin{aligned}
 \theta^{(11)} + H \left\{ -\frac{2}{\alpha^2} e^{-\alpha \eta} (1-E^{(o)}) \eta^{m-2-4\beta/E^{(o)}} \right. \\
 + \frac{2C_1 (1-E^{(o)}) \eta^{m+1-6\beta/E^{(o)}}}{(E^{(o)})^2 (m-6\beta/E^{(o)}) (m+1-6\beta/E^{(o)})} + \frac{4C_2 (1-E^{(o)}) \eta^{m-5\beta/E^{(o)}}}{(E^{(o)})^2 (m-5\beta/E^{(o)}) (m-1-5\beta/E^{(o)})} \\
 \left. + 2 \left( \frac{F^{(10)}}{E^{(o)}} \right) \frac{(1-E^{(o)}) \eta^{m-1-4\beta/E^{(o)}}}{(m-2-4\beta/E^{(o)}) (m-1-4\beta/E^{(o)})} - F^{(11)} \eta \right\} = -E^{(11)} + G^{(11)}
 \end{aligned} \tag{69}$$

The boundary conditions are:

$$\theta^{(11)}(0) = \theta^{(11)}(1) = 0 .$$

Therefore:

$$\begin{aligned}
 G^{(11)} = H \left\{ -\frac{2}{\alpha^2} + \frac{2C_1}{(E^{(o)})^2 (m-6\beta/E^{(o)}) (m+1-6\beta/E^{(o)})} \right. \\
 \left. + \frac{4C_2}{(E^{(o)})^2 (m-5\beta/E^{(o)}) (m-1-5\beta/E^{(o)})} + 2 \left( \frac{F^{(10)}}{E^{(o)}} \right)^2 \frac{1}{(m-2-4\beta/E^{(o)}) (m-1-4\beta/E^{(o)})} \right\}
 \end{aligned}$$

$$\begin{aligned}
 E^{(11)} = H \left\{ -\frac{2}{\alpha^2} \left[ 1 - e^{-\alpha} (1-E^{(o)})^{m-2-4\beta/E^{(o)}} \right] \right. \\
 + \frac{2C_1 \left[ 1 - (1-E^{(o)})^{m+1-6\beta/E^{(o)}} \right]}{(E^{(o)})^2 (m-6\beta/E^{(o)}) (m+1-6\beta/E^{(o)})} + \frac{4C_2 \left[ 1 - (1-E^{(o)})^{m-5\beta/E^{(o)}} \right]}{(E^{(o)})^2 (m-5\beta/E^{(o)}) (m-1-5\beta/E^{(o)})} \\
 + 2 \left( \frac{F^{(10)}}{E^{(o)}} \right)^2 \frac{\left[ 1 - (1-E^{(o)})^{m-1-4\beta/E^{(o)}} \right]}{(m-2-4\beta/E^{(o)}) (m-1-4\beta/E^{(o)})} + \frac{E^{(o)} (1-\beta/E^{(o)})}{\left[ 1 - (1-E^{(o)})^{1-\beta/E^{(o)}} \right]} \\
 \left. + \left[ \frac{2}{\alpha^2} \left[ 1 - e^{-\alpha} (1-E^{(o)})^{m-2-5\beta/E^{(o)}} \right] - \frac{2C_1 \left[ 1 - (1-E^{(o)})^{m+1-7\beta/E^{(o)}} \right]}{(E^{(o)})^2 (m-6\beta/E^{(o)}) (m+1-7\beta/E^{(o)})} - \right. \right.
 \end{aligned}$$

$$- \frac{4C_2 [1 - (1-E^{(o)})] m-6\beta/E^{(o)}}{(E^{(o)})^2 (m-6\beta/E^{(o)}) (m-1-5\beta/E^{(o)})} - 2 \left( \frac{F^{(10)}}{E^{(o)}} \right)^2 \frac{[1 - (1-E^{(o)}) m-1-5\beta/E^{(o)}]}{(m-2-4\beta/E^{(o)}) (m-1-5\beta/E^{(o)})} \right] \Bigg\} \quad (70)$$

Since  $\alpha \gtrsim 4$  ordinarily,  $e^{-\alpha}$  can usually be neglected compared with one. Furthermore, it has already been mentioned that  $E^{(o)} \ll 1$  in most cases, and if this is true, the binomial expressions in  $E^{(o)}$  can be expanded to yield a simpler, approximate equation in place of equation 70:

$$E^{(11)} = - H\beta \left[ \frac{1}{\alpha^2} + \frac{C_1}{6} \frac{\left[ 1 + \frac{7}{2} \left( \beta - \frac{mE^{(o)}}{7} \right) \right]}{\left( \beta - \frac{mE^{(o)}}{6} \right)} + \frac{2C_2}{5} \frac{\left[ 1 + 3 \left( \beta - \frac{(m-1)E^{(o)}}{3} \right) \right]}{\left( \beta - \frac{(m-1)E^{(o)}}{5} \right)} + \frac{(F^{(10)})^2}{4} \frac{\left[ 1 + \frac{5}{2} \left( \beta - \frac{2(m-2)E^{(o)}}{5} \right) \right]}{\left( \beta - \frac{(m-2)E^{(o)}}{4} \right)} \right] \quad (71)$$

As reactions begin to occur and the gas tends away from a completely frozen state, the energy transfer is affected (to order  $O(\epsilon\delta)$ ) only in the presence of a pressure gradient, if the walls are catalytic.

### Non-Catalytic Walls

In this case, there are no reactions at the wall surfaces, and every atom or molecule that strikes the wall rebounds into the flow unchanged. The corresponding boundary condition is that the diffusion flux vanishes at both walls. From equations 58 and 59 then:

$$\frac{dx^{(10)}}{d\eta} + \frac{\beta x^{(10)}}{1-E^{(o)}\eta} = - \Gamma^{(10)} = 0$$

and

$$x^{(10)} = F^{(10)}(1 - E^{(0)}\eta)^{\beta/E^{(0)}}. \quad (72)$$

Since  $\Gamma^{(10)} = 0$ , the energy equation yields:

$$-\frac{d\theta^{(10)}}{d\eta} = E^{(10)}.$$

The temperature boundary conditions are again satisfied exactly by the zeroth-order energy equation, so that  $\theta^{(10)}(0) = \theta^{(10)}(1) = 0$ . Therefore,  $\theta^{(10)} = 0$  everywhere, and

$$E^{(10)} = 0. \quad (73)$$

With non-catalytic walls, there is no first-order effect on the heat transfer due to a small degree of dissociation, if the mixture is completely frozen.

To examine the effect of reaction rate with non-catalytic walls, equation 72 can be used to eliminate  $x^{(10)}$  from equation 60:

$$\frac{d\Gamma^{(11)}}{d\eta} = 2e^{-\alpha\eta} (1 - E^{(0)}\eta)^{m-2-4\beta/E^{(0)}} - 2(F^{(10)})^2 (1 - E^{(0)}\eta)^{m-3-4\beta/E^{(0)}}.$$

Therefore:

$$\Gamma^{(11)} = -\frac{2}{\alpha} e^{-\alpha\eta} (1 - E^{(0)}\eta)^{m-2-4\beta/E^{(0)}} + \frac{2(F^{(10)})^2 (1 - E^{(0)}\eta)^{m-2-4\beta/E^{(0)}}}{E^{(0)}(m-2-4\beta/E^{(0)})} + K^{(11)}. \quad (74)$$

Since  $E^{(0)} \ll 1$  and  $\alpha \gtrsim 4$ , terms  $O(E^{(0)}/\alpha^2)$  have been neglected here. The boundary conditions are  $\Gamma^{(11)}(0) = \Gamma^{(11)}(1) = 0$ . Thus:

$$K^{(11)} = \frac{2}{\alpha} - \frac{2(F^{(10)})^2}{E^{(0)}(m-2-4\beta/E^{(0)})}$$

$$(F^{(10)})^2 = \frac{E^{(0)}}{\alpha} \left[ 1 - e^{-\alpha(1-E^{(0)})^{m-2-4\beta/E^{(0)}}} \right] \cdot \left[ \frac{(1-E^{(0)})^{m-2-4\beta/E^{(0)}}}{1 - (1-E^{(0)})^{m-2-4\beta/E^{(0)}}} \right] \quad (75)$$

The energy equation is:

$$-\frac{d\theta^{(11)}}{d\eta} + H\Gamma^{(11)} = E^{(11)}$$

where  $\Gamma^{(11)}$  is provided by equation 74. Integration gives:

$$\begin{aligned} \theta^{(11)} + 2H \left\{ -\frac{e^{-\alpha\eta}}{\alpha^2} (1-E^{(0)})^{m-2-4\beta/E^{(0)}} \right. \\ \left. + \left( \frac{F^{(10)}}{E^{(0)}} \right)^2 \frac{(1-E^{(0)})^{m-1-4\beta/E^{(0)}}}{(m-1-4\beta/E^{(0)})(m-2-4\beta/E^{(0)})} + \left[ \frac{(F^{(10)})^2}{E^{(0)}(m-2-4\beta/E^{(0)})} - \frac{1}{\alpha} \right] \eta \right\} \\ = -E^{(11)}\eta + F^{(11)} \end{aligned} \quad (76)$$

The integration constant  $F^{(11)}$  and the eigenvalue  $E^{(11)}$  are determined by the boundary conditions,  $\theta^{(11)}(0) = \theta^{(11)}(1) = 0$  :

$$\begin{aligned} F^{(11)} &= 2H \left[ \frac{(F^{(10)})^2}{E^{(0)}(m-2-4\beta/E^{(0)})} - \frac{1}{\alpha} \right] \\ E^{(11)} &= \frac{2H}{\alpha} \left\{ 1 - \alpha \left( \frac{F^{(10)}}{E^{(0)}} \right)^2 \frac{[(1-E^{(0)})^{m-1-4\beta/E^{(0)}} - 1]}{(m-1-4\beta/E^{(0)})(m-2-4\beta/E^{(0)})} \right. \\ &\quad \left. - \alpha \left( \frac{F^{(10)}}{E^{(0)}} \right)^2 \frac{E^{(0)}}{(m-2-4\beta/E^{(0)})} - \frac{1}{\alpha} \left[ 1 - e^{-\alpha(1-E^{(0)})^{m-2-4\beta/E^{(0)}}} \right] \right\} \end{aligned} \quad (77)$$

If  $e^{-\alpha}$  is negligible compared with 1 and  $E^{(0)} \ll 1$ , a simpler approximate expression can be obtained from equation 77 as before:

$$E^{(11)} \approx \frac{H}{\alpha} \left[ 1 - \frac{2}{\alpha} + \frac{(3-m)E^{(0)} + 4\beta}{2} \right] \quad (78)$$

This equation shows that with non-catalytic walls there is an appreciable increase in the heat transfer as the gas departs from a completely frozen state, whether or not there is a pressure gradient.

#### A Numerical Example: Bromine Dissociation

To illustrate the results obtained for the near-frozen case, a numerical example has been calculated for bromine dissociation. Very good agreement between equation 55 and tabulated values of the equilibrium constant  $(21)^*$  is obtained by letting  $\theta_a = 22.5$ . The hot wall is assumed to have a temperature  $T_0 = 1500^\circ\text{K}$  and a pressure  $p_0 = 1.0$  atm. Then according to equation 53,  $\epsilon = 0.298$ . This means that if the walls are perfectly catalytic, the mole fraction of atomic bromine at the hot wall is 0.298. It is also assumed that the temperature ratio at the cold wall  $T_1/T_0 = 0.75$ , i.e. the cold wall is maintained at  $1125^\circ\text{K}$ . In this calculation,  $\beta \geq 0$ , which means that energy transport by pressure diffusion tends to counteract ordinary heat conduction, because the temperature gradient and pressure gradient are oppositely oriented.

The results for completely frozen flow ( $\delta = 0$ ) are shown in figure 1. When the walls are catalytic the gas behaves like a mixture of inert species except at the wall surfaces, where the catalytic effect causes reactions which drive the composition to local chemical equilibrium at the surface temperature. As figure 1 shows, there is an appreciable pres-

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\* The tabulated equilibrium constant, given in terms of partial pressures, is converted to the equilibrium constant in terms of concentrations by means of the perfect gas equation of state (22).

sure-gradient effect, amounting to a 23 per cent reduction in the energy transport as  $\beta$  reaches 0.75. This corresponds to a pressure ratio across the channel of about 5 to 1, i.e. the pressure at the cold wall is about 5 atm. To interpret this, it is worthwhile to note that if the radius of curvature were on the order of ten times the channel width in an enclosure comprising two concentric cylinders, such a pressure ratio would be achieved with Mach numbers of 2 to 3. This would be a case where the channel-flow approximation would be quite reasonable. With a relatively small radius of curvature the present analysis could not be expected to yield accurate quantitative results, but it should still give a reasonable indication of the relative magnitude of the pressure effect, and in this case, the pressure ratio of 5 to 1 would be achieved at subsonic Mach numbers.

It should also be remembered that figure 1 corresponds to a maximum degree of dissociation of about 30 per cent ( $\epsilon = 0.298$  at the hot wall). Again, the linearized analysis is not strictly valid for much greater dissociation, but it can give some indication of relative magnitudes for such cases. Thus, if the mole fraction of atomic bromine at the hot wall were doubled to about 0.6 (corresponding to a temperature increase of only about  $150^\circ\text{K}$ , i.e. from  $1500^\circ\text{K}$  to approximately  $1650^\circ\text{K}$ ), the total energy transport would increase by about 50 per cent, and a pressure ratio of 5 to 1 would reduce the energy transport by roughly 40 per cent (assuming the same temperature ratio between walls as in figure 1).

Since there are no reactions in the flow except at the wall surfaces, the pressure effect illustrated by figure 1 is a direct result of the pressure gradient, or in other words, it is due to pressure diffusion alone.



Because of concentration diffusion, atoms tend to travel from the hot wall toward the cold wall, carrying thermal and chemical energy, but pressure diffusion opposes this transport. Of course, if the temperature gradient and pressure gradient were in the same direction, energy transport would be enhanced by pressure diffusion, rather than retarded as in figure 1.

The same figure shows the energy transport when the walls are non-catalytic and the gas is chemically frozen. In this case, the diffusion flux must vanish everywhere to satisfy the continuity equation and the boundary conditions. Energy transport is therefore by thermal conduction alone, so there can be no pressure gradient effect.

The effect of non-zero chemical reaction rates is illustrated in figure 2. There is no general agreement on the temperature dependence of the collision frequency factor  $Z$  for three-body recombination, so the quantity  $m$  (defined by equation 46) is arbitrarily chosen as zero for figure 2. The results are nearly independent of  $m$  anyway.

The analysis of chemical equilibrium flow in the next section shows that for given temperature and pressure boundary conditions and catalytic walls, the energy transfer is the same (to  $O(\epsilon)$ ) whether the flow is in equilibrium or frozen, provided there is no pressure gradient ( $\beta = 0$ ). This is not very surprising, because with no pressure gradient only concentration diffusion occurs, and if the composition is in local equilibrium at both walls the average concentration gradient between the walls is approximately the same whether the flow is frozen or in equilibrium. It follows that in the absence of a pressure gradient there is no first-order change in the heat transfer as the mixture departs from a

frozen state (or an equilibrium state), if the walls are catalytic. This is shown by equation 71 and reflected in the curves of figure 2 for catalytic walls.

If there is a pressure gradient, a rate effect exists with catalytic walls. This is an "indirect" result of the pressure gradient, since it is really due primarily to the effect of local pressure (which is a function of  $\beta$ ) on the recombination reaction rate. For a given pressure at the hot wall, a higher pressure gradient provides a greater density near the cold wall. This increases the recombination reaction rate due to the more frequent three-body collisions involving two atoms. As explained before, the recombination reactions act as heat sources, reducing the total energy transport between the walls for given temperature boundary conditions. An increase in the pressure gradient therefore has the net effect of intensifying the reduction in energy transport which accompanies a departure from the frozen state.

This argument implies that the recombination reaction will predominate over dissociation when the gas mixture departs from equilibrium. This is the case, because in a frozen state the atomic mole fraction varies almost linearly between the local equilibrium values at the catalytic walls (see equation 61), while it has an exponential character (equation 62) when the gas is in chemical equilibrium. As shown in figure 3, the equilibrium mole fraction of atoms at any point in the flow is less than the frozen mole fraction, except at the walls, of course, where they are the same if the surfaces are catalytic. Therefore, as the flow departs from a chemically frozen state recombination predominates, since the composition tends toward local chemical equilibrium.

Figure 2 also shows that with non-catalytic walls the energy transport increases as the flow leaves the chemically frozen state. The increase is due to diffusion, which is not present in the frozen flow. In this case, the recombination reaction does not predominate everywhere. The equilibrium composition with non-catalytic walls again has the exponential character of the equilibrium constant, except very near the walls, as shown in the next section. The frozen composition is given by equation 72; at every point the concentration diffusion just balances the pressure diffusion so that there is no net diffusion, and the mole fraction falls between the equilibrium values at the cold and hot walls. This situation is illustrated in figure 4.

As the gas departs from the frozen state, the reactions tend to drive the composition toward local equilibrium, which results in an increased concentration gradient. This in turn leads to concentration diffusion (except at the walls, where the diffusion flux must vanish) and the consequent increase in energy transport indicated by figure 2. The effect is intensified by a pressure gradient, and this is again an indirect effect due to the influence of density on the local reaction rate. For example, a higher pressure near the cold wall (corresponding to a greater value of  $\beta$ ) enhances the recombination and steepens the concentration gradient. This strengthens the increase in energy transport with a departure from frozen flow.

## V. CHEMICAL EQUILIBRIUM AND NEAR-EQUILIBRIUM FLOW OF THE BINARY GAS

In this section the extreme opposite from frozen flow, in the sense of chemical reaction kinetics, is considered. Although the recombination reaction associated with simple dissociation involves a three-body collision, in many cases there may be a close approach to local chemical equilibrium in the gas mixture. This implies that the reaction rate is very fast relative to the diffusion rate, so that atoms or molecules travel through only a short distance between reactions, and the equilibrium concentrations at the local temperature are closely approached. This situation will prevail if, for example, the gas density is high, making three-body collisions relatively frequent. More precisely, the criterion for a close approach to local chemical equilibrium is that  $R \gg 1$  in equation 46, since the rate parameter  $R$  is essentially the ratio of reaction rate to diffusion rate. This restriction forms the basis for a perturbation treatment similar to that given for near-frozen flow, where the expansion parameter is now  $1/\epsilon R$  rather than  $\epsilon R$ .

It is shown in Appendix A that when a binary reacting mixture is very nearly in local chemical equilibrium the energy flux can be described by a generalized Fourier equation. The effective coefficient of thermal conductivity, given by equation 161, includes the influence of chemical reactions and diffusion. Formally, the binary gas in chemical equilibrium is like a single-component gas, since the diffusion equation need not be included in the mathematical formulation of the problem. In either the single-component or binary case, the required conservation equations are the continuity equation, momentum equation, and the energy equation (using the effective coefficient of thermal conductivity in the binary case).

The order of the system of equations is the same in both cases. Hirschfelder (5) indicated that a similar effective coefficient of thermal conductivity could be defined for a mixture in equilibrium at constant pressure, but equation 161 shows that this generalized Fourier law is valid for a binary mixture even when a strong pressure gradient is present. It cannot be concluded that a pressure gradient in the gas will have no influence on the energy transport, however. The effective thermal conductivity is a function of the pressure as well as the temperature. Therefore, for a given pressure level at an arbitrary point in the flow, changes in the pressure gradient will influence the energy transport.

Hirschfelder (5) has pointed out that even if the main body of the mixture is nearly in local chemical equilibrium, there may be large deviations from equilibrium near the wall surfaces. This is particularly evident when the walls are non-catalytic, for example. If the surfaces are completely inert, the diffusion velocities of both species must vanish at the walls. However, the presence of a temperature gradient and local chemical equilibrium will lead to non-zero diffusion velocities. Therefore, in the neighborhood of the wall, the diffusion velocities must adjust from their non-zero values in the main stream to meet the boundary condition. In this adjustment region second derivatives of the diffusion velocity, which are usually negligible in the main stream where the gas is nearly in equilibrium, may become large and have to be considered. Thus, in the neighborhood of the wall the order of the system of differential equations is effectively raised, and by analogy to the viscous boundary layer, the adjustment region can be called a reaction boundary layer.

Large changes in the diffusion velocity within the boundary layer do not necessarily imply that the composition deviates extensively from

chemical equilibrium at the wall. According to the diffusion equation, the concentration gradient may change considerably along with the diffusion velocity, but if the boundary layer is thin, the composition itself should remain nearly in equilibrium throughout the layer. The thickness of the boundary layer is the average distance molecules or atoms starting at the wall will cover through diffusion before reactions have brought the composition into local equilibrium. If the reaction rate is large compared with the diffusion rate, the layer will be thin. The criteria for a close approach to chemical equilibrium in the main stream, and for thin boundary layers containing moderate departures from the equilibrium composition, are therefore identical.

The treatment of a simple dissociating gas which is nearly in chemical equilibrium is similar to that for frozen flow in the last section. However, it can be observed at the outset that the classical perturbation technique will not yield a uniformly valid result throughout the channel because of the reaction boundary layers. Since certain derivatives which are negligible in the main stream may become important near the walls, the perturbation is singular at the walls, and a special treatment is required in the boundary layers.

The dependent variables and energy transport eigenvalue are again expressed in two-parameter expansions:

$$\begin{aligned}
 \theta &= \theta^{(0)} + \epsilon(\theta^{(10)} + \xi\theta^{(11)} + \dots) + O(\epsilon^2) + O(\xi^2) \\
 x &= 0 + \epsilon(x^{(10)} + \xi x^{(11)} + \dots) + O(\epsilon^2) + O(\xi^2) \\
 \Gamma &= 0 + \epsilon(\Gamma^{(10)} + \xi\Gamma^{(11)} + \dots) + O(\epsilon^2) + O(\xi^2) \\
 E &= E^{(0)} + \epsilon(E^{(0)} + \xi E^{(11)} + \dots) + O(\epsilon^2) + O(\xi^2)
 \end{aligned} \tag{85}$$

where  $\epsilon$  is still defined by equation 53 and

$$\xi = 1/\epsilon R \ll 1 . \quad (86)$$

It is therefore implied by the expansion that "near-equilibrium" here means:

$$1/R \ll \epsilon \ll 1 .$$

As in the frozen flow case, the zeroth-order solution is given by equation 50 and higher order energy equations by equation 57. The diffusion equations are again given by 58. The basic difference between the two cases appears in the continuity equation, because the rate parameter appears there. Substituting equations 85 into that equation and equating coefficients of equal order in  $\epsilon$  and  $\xi$  leads to:

$$(x^{(10)})^2 = e^{-\alpha\eta} \frac{\theta^{(0)}}{\pi} = e^{-\alpha\eta} (1-E^{(0)}\eta)^{1+2\beta/E^{(0)}} \quad (87)$$

$$\frac{d\Gamma^{(10)}}{d\eta} = - \left[ 4x^{(10)} \left( \frac{\pi}{\theta^{(0)}} \right)^{3+m} \right] x^{(11)} = - \left[ 4e^{-\frac{\alpha\eta}{2}} (1-E^{(0)}\eta)^{n-\frac{5}{2}-5\beta/E^{(0)}} \right] x^{(11)} \quad (88)$$

### Perfectly Catalytic Walls

When the walls are perfectly catalytic, driving the composition to chemical equilibrium at their surfaces, the boundary conditions to be applied on  $x$  are obtained by substituting the expansions 85 into the expression

$$\frac{x^2}{1-x} = \frac{\theta}{\pi} \frac{K_n}{n_o}$$

where  $K_n/n_o$  is given by equation 55. Equation 87 corresponds to an infinite reaction rate ( $\xi = 0$ ), so it satisfies the  $O(\epsilon)$  catalytic wall boundary conditions automatically.

From equation 87:

$$\frac{dx^{(10)}}{d\eta} = -\frac{1}{2} \left( \alpha + \frac{E^{(o)}}{1-E^{(o)}\eta} \right) x^{(10)} - \frac{\beta x^{(10)}}{1-E^{(o)}\eta},$$

and the diffusion equation gives:

$$\Gamma^{(10)} = -\frac{dx^{(10)}}{d\eta} + \frac{\beta x^{(10)}}{1-E^{(o)}\eta} = \frac{1}{2} \left( \alpha + \frac{E^{(o)}}{1-E^{(o)}\eta} \right) x^{(10)}. \quad (89)$$

This equation again demonstrates that the diffusion velocity can be written in terms of the local pressure, temperature, and temperature gradient when the binary mixture is in chemical equilibrium. (Note that  $\alpha = \theta_a E^{(o)}$ , and  $E^{(o)} = -d\theta^{(o)}/d\eta$ ;  $x^{(10)} = x^{(10)}(T, p)$ .) However, from equation 87:

$$\Gamma^{(10)} = \frac{1}{2} \left( \alpha + \frac{E^{(o)}}{1-E^{(o)}\eta} \right) e^{-\frac{\alpha\eta}{2}} (1-E^{(o)}\eta)^{\frac{1}{2}} + \beta/E^{(o)}. \quad (90)$$

As mentioned before, the diffusion flux is affected by the pressure gradient to the extent that the local pressure depends on  $\beta$ .

The  $O(\epsilon)$  energy equation is

$$-\frac{d\theta^{(10)}}{d\eta} + H\Gamma^{(10)} = E^{(10)}$$

where  $\Gamma^{(10)}$  is given by equation 90. Integrating and retaining terms  $O(E^{(o)}/\alpha)$  but not  $O(E^{(o)}/\alpha)^2$ :

$$-\theta^{(10)} - H \left[ 1 - \frac{2\beta}{(1-E^{(o)}\eta)} \right] e^{-\frac{\alpha\eta}{2}} (1-E^{(o)}\eta)^{\frac{1}{2}} + \beta/E^{(o)} = E^{(10)}\eta + F^{(10)} \quad (91)$$

The boundary conditions are  $\theta^{(10)}(0) = \theta^{(10)}(1) = 0$ . Therefore:

$$F^{(10)} = -H \left[ 1 - \frac{2\beta}{\alpha} \right]$$



$$E^{(10)} = H \left\{ 1 - e^{-\frac{\alpha}{2} (1-E^{(0)})^{\frac{1}{2} + \beta/E^{(0)}}} - \frac{2\beta}{\alpha} \left[ 1 - e^{-\frac{\alpha}{2} (1-E^{(0)})^{-\frac{1}{2} + \beta/E^{(0)}}} \right] \right\} \quad (92)$$

A comparison of equations 65 and 92 shows that with catalytic walls the energy transfer is the same to  $O(\epsilon)$  whether the flow is frozen or in equilibrium, if there is no pressure gradient.

Equation 88 is the starting point for an examination of the effect of small departures from local equilibrium. The derivative  $d\Gamma^{(10)}/d\eta$  is obtained from equation 90; thus:

$$\begin{aligned} \frac{d\Gamma^{(10)}}{d\eta} = -\frac{1}{4} \left\{ \alpha \left[ \alpha + \frac{2(E^{(0)} + \beta)}{1-E^{(0)}\eta} \right] - \frac{E^{(0)}(E^{(0)} - 2\beta)}{(1-E^{(0)}\eta)^2} \right\} \\ \cdot e^{-\frac{\alpha\eta}{2} (1-E^{(0)}\eta)^{\frac{1}{2} + \beta/E^{(0)}}} \end{aligned} \quad (93)$$

After substitution of 93, equation 88 is an algebraic expression for  $x^{(11)}$  and is therefore incapable of satisfying the boundary conditions for catalytic walls,  $x^{(11)}(0) = x^{(11)}(1) = 0$ . This occurs because the perturbation technique neglects derivatives of  $x^{(11)}$ , which appear in  $d\Gamma^{(11)}/d\eta$ . It is a singular perturbation, failing because  $x^{(11)}$  has a boundary layer character such that in the neighborhood of the boundaries the neglected derivatives, particularly  $d^2x^{(11)}/d\eta^2$ , grow to the same order of magnitude as terms in equation 88.

If the neglected term  $d\Gamma^{(11)}/d\eta$  is included and evaluated in terms of  $x^{(11)}$  from the diffusion equation, the equation which is valid throughout the channel and capable of satisfying boundary conditions is:

$$\begin{aligned} \frac{d^2 x^{(11)}}{d\eta^2} + \frac{\beta}{\theta^{(0)}} \frac{dx^{(11)}}{d\eta} + \left[ \frac{\beta E^{(0)}}{(\theta^{(0)})^2} - \frac{4}{\xi} \left( \frac{\pi}{\theta^{(0)}} \right)^{\frac{5}{2}} (\theta^{(0)})^m e^{-\frac{\alpha\eta}{2}} \right] x^{(11)} \\ = -\frac{1}{4\xi} \left\{ \alpha \left[ \alpha + \frac{2(E^{(0)} + B)}{\theta^{(0)}} \right] - \frac{E^{(0)}(E^{(0)} - 2\beta)}{(\theta^{(0)})^2} \right\} \left( \frac{\theta^{(0)}}{\pi} \right)^{\frac{1}{2}} e^{-\frac{\alpha\eta}{2}} \end{aligned} \quad (94)$$

where  $\theta^{(0)} = (1 - E^{(0)}\eta)$  and  $\pi = (1 - E^{(0)}\eta)^{-2\beta/E^{(0)}}$ . It is expected that the derivatives are important only near the walls, so that this reduces to equation 88 in the main stream. In principle, equation 94 can be solved, because it is linear with variable coefficients. However, this is impractical because of the very complicated coefficients. For example, if the solution were in terms of a power series in  $\eta$ , many terms would be required to accurately describe the rapidly changing behavior near  $\eta = 0$  and  $\eta = 1$  combined with a slowly varying character in the main stream.

Instead, it is convenient to divide the flow into three regions: the main stream, where the solution is given by equation 88; and the two boundary layers, where the second derivative is important. This procedure implies that the solution has a true boundary layer character, i. e. that the main stream solution is independent of the boundary conditions. To demonstrate that this is reasonable, it is helpful to consider a simpler equation which retains the character of 94. The dominating variable in the coefficients of equation 94 is the exponential, which for realistic values of  $\alpha$  can change by a factor of  $10^2$  or more in the range of  $0 \leq \eta \leq 1$ . Therefore consider:

$$\frac{d^2 x}{d\eta^2} - \left[ \frac{C_1 e^{-\frac{\alpha\eta}{2}}}{\xi} \right] x = -\frac{C_2 e^{-\frac{\alpha\eta}{2}}}{\xi} \quad 0 \leq \eta \leq 1$$

where the boundary conditions are  $x(0) = a$  and  $x(1) = b$ , and  $C_1$  and

$C_2$  are constants. A new independent variable is defined by

$$s = -\frac{4}{\alpha} e^{-\frac{\alpha\eta}{4}}$$

and this simplifies the equation to one having constant coefficients:

$$\frac{d^2 x}{ds^2} - \frac{C_1}{\xi} x = -\frac{C_2}{\xi} \quad \begin{aligned} x(-\frac{4}{\alpha}) &= a \\ x(-\frac{4}{\alpha} e^{-\alpha/4}) &= b \end{aligned}$$

For  $\xi \ll 1$ , which is the case of interest here, the solution reduces to:

$$x = (a - \frac{C_2}{C_1}) e^{-\sqrt{\frac{C_1}{\xi}} \frac{4}{\alpha} (1 - e^{-\frac{\alpha\eta}{4}})} + (b - \frac{C_2}{C_1}) e^{-\sqrt{\frac{C_1}{\xi}} \frac{4}{\alpha} (e^{-\frac{\alpha\eta}{4}} - e^{-\frac{\alpha}{4}})} + \frac{C_2}{C_1}.$$

If the  $\alpha$ ,  $C_1$ , and  $\xi$  appearing here are associated with the corresponding quantities in equation 94, typical values would be  $\alpha \sim 4$  and  $C_1/\xi \gtrsim 10^2$ . Therefore, if  $(a - C_2/C_1)$  and  $(b - C_2/C_1)$  are negligible compared with  $e^{+\sqrt{C_1/\xi}}$ ,  $x \approx C_2/C_1$  except near the boundaries, regardless of the boundary conditions  $a$  and  $b$ . This conclusion is also appropriate to equation 88.

Returning now to equation 94, to find the boundary layer behavior at the hot wall ( $\eta = 0$ ) it is convenient to define a new independent variable:

$$z = \eta/\xi^{\frac{1}{2}}$$

Then neglecting terms  $O(\xi^{\frac{1}{2}})$  or smaller, 94 becomes:

$$\frac{d^2 x^{(11)}}{dz^2} - 4x^{(11)} = -C \quad (94a)$$

where  $C = \frac{1}{4} \{ \alpha [\alpha + 2(E^{(o)} + \beta)] - E^{(o)}(E^{(o)} + \beta) \}$ . The boundary conditions are:

$$\begin{aligned} z = 0 : \quad x^{(11)} &= 0 \\ z \longrightarrow \infty : \quad x^{(11)} &= C/4 \text{ (given by equation 88 at } \eta = 0). \end{aligned}$$

Therefore, in the boundary layer at the hot wall:

$$x^{(11)} = \frac{1}{16} \left\{ \alpha [\alpha + 2(E^{(0)} + \beta)] - E^{(0)}(E^{(0)} - 2\beta) \right\} \left[ 1 - e^{-2\eta/\xi^{\frac{1}{2}}} \right]. \quad (95)$$

Similarly, at the cold wall:

$$x^{(11)} = \frac{(1-E^{(0)})^{3-m+6\beta/E^{(0)}}}{16} \left\{ \alpha \left[ \alpha + \frac{2(E^{(0)} + \beta)}{1-E^{(0)}\eta} \right] - \frac{E^{(0)}(E^{(0)} - 2\beta)}{(1-E^{(0)}\eta)^2} \right\} [ ] \quad (96)$$

where:

$$[ ] = \left[ 1 - e^{-2\eta/\xi^{\frac{1}{2}}} - e^{-\frac{2(1-E^{(0)})^{\frac{1}{2}}(m-\frac{5}{2}-5\beta/E^{(0)})e^{-\alpha/4}(1-\eta)}{\xi^{\frac{1}{2}}}} \right].$$

From equations 88, 93, 95 and 96, a composite approximate solution can be formed which is valid throughout the channel for  $\xi \ll 1$ :

$$x^{(11)} = \frac{(1-E^{(0)})^{3-m+6\beta/E^{(0)}}}{16} \left\{ \alpha \left[ \alpha + \frac{2(E^{(0)} + \beta)}{1-E^{(0)}\eta} \right] - \frac{E^{(0)}(E^{(0)} - 2\beta)}{(1-E^{(0)}\eta)^2} \right\} [ ] \quad (97)$$

where:

$$[ ] = \left[ 1 - e^{-2\eta/\xi^{\frac{1}{2}}} - e^{-\frac{2(1-E^{(0)})^{\frac{1}{2}}(m-\frac{5}{2}-5\beta/E^{(0)})e^{-\alpha/4}(1-\eta)}{\xi^{\frac{1}{2}}}} \right].$$

Since  $E^{(0)} \ll \alpha$  and  $\beta \ll \alpha$ , the third term in the first bracket can be neglected. In the main stream, where the exponentials of equation 97 are unimportant:

$$\begin{aligned} \frac{dx^{(11)}}{d\eta} &= \frac{\alpha^2 E^{(0)}}{16} (m-3-6\beta/E^{(0)})(1-E^{(0)}\eta)^{2-m+6\beta/E^{(0)}} \\ &- \frac{\alpha}{4} \left[ \left(1-\frac{m}{2}\right)E^{(0)} + 3\beta \right] (E^{(0)} + \beta)(1-E^{(0)}\eta)^{1-m+6\beta/E^{(0)}} . \end{aligned}$$

When this expression is substituted into equation 58, the diffusion equation, the result is:

$$\begin{aligned} \Gamma^{(11)} &= \frac{\alpha^2}{16} \left[ (3-m)E^{(0)} + 5\beta \right] (1-E^{(0)}\eta)^{2-m+6\beta/E^{(0)}} \\ &+ \frac{\alpha}{8} \left[ (2-m)(E^{(0)})^2 + 5\beta^2 + (7-m)\beta E^{(0)} \right] (1-E^{(0)})^{1-m+6\beta/E^{(0)}} . \end{aligned}$$

This in turn can be substituted into the energy equation, given by equation 57, and integration yields:

$$\begin{aligned} -\theta^{(11)} - H &\left\{ \frac{\alpha^2}{16} \frac{(3-m+5\beta/E^{(0)})(1-E^{(0)}\eta)^{3-m+6\beta/E^{(0)}}}{(3-m+6\beta/E^{(0)})} \right. \\ &+ \frac{\alpha E^{(0)}}{8} \left[ (2-m) + (7-m)\beta/E^{(0)} + 5(\beta/E^{(0)})^2 \right] (1-E^{(0)})^{1-m+6\beta/E^{(0)}} \Big\} \\ &= E^{(11)}\eta + F^{(11)} . \end{aligned} \quad (98)$$

Applying the boundary conditions:

$$\begin{aligned} F^{(11)} &= -\theta^{(11)}(0) - H \left\{ \frac{\alpha^2}{16} \frac{(3-m+5\beta/E^{(0)})}{(3-m+6\beta/E^{(0)})} \right. \\ &+ \frac{\alpha E^{(0)}}{8} \frac{[2-m+(7-m)\beta/E^{(0)}+5(\beta/E^{(0)})^2]}{(2-m+6\beta/E^{(0)})} \Big\} \end{aligned}$$

$$\begin{aligned}
 E^{(11)} = & \theta^{(11)}(0) - \theta^{(11)}(1) + H \left\{ \frac{\alpha}{16} \left( \frac{3-m+5\beta/E^{(0)}}{3-m+6\beta/E^{(0)}} \right)^2 \right. \\
 & \cdot \left[ 1 - (1-E^{(0)})^{3-m+6\beta/E^{(0)}} \right] + \frac{\alpha E^{(0)}}{8} \frac{[2-m+(7-m)\beta/E^{(0)} + 5(\beta/E^{(0)})^2]}{(2-m+6\beta/E^{(0)})} \\
 & \cdot \left. \left[ 1 - (1-E^{(0)})^{2-m+6\beta/E^{(0)}} \right] \right\} . \quad (99)
 \end{aligned}$$

The main-stream boundary conditions,  $\theta^{(11)}(0)$  and  $\theta^{(11)}(1)$ , are found by integrating the energy equation through the boundary layers. Using equation 58 to eliminate  $\Gamma^{(11)}$ , the energy equation is:

$$- \frac{d\theta^{(11)}}{d\eta} - H \left( \frac{dx^{(11)}}{d\eta} + \frac{\beta x^{(11)}}{1-E^{(0)}\eta} \right) = E^{(11)} .$$

As equations 95 and 96 show, the appropriate length scales in the hot and cold boundary layers are  $\eta/\xi^{\frac{1}{2}}$  and  $(1-\eta)/\xi^{\frac{1}{2}}$ , respectively. If  $z = \eta/\xi^{\frac{1}{2}}$  and terms  $O(\xi^{\frac{1}{2}})$  are neglected, the energy equation in the boundary layer at the hot wall is:

$$\frac{d\theta^{(11)}}{dz} + H \frac{dx^{(11)}}{dz} = 0 ;$$

or, since  $\theta^{(11)}(0) = x^{(11)}(0) = 0$ ,

$$\theta^{(11)}(z \rightarrow \infty) = -H x^{(11)}(z \rightarrow \infty) .$$

This gives the boundary condition on the temperature in the free stream; i. e. in equation 99,  $\theta^{(11)}(\eta = 0) = -H x^{(11)}(\eta = 0)$ . Similarly, at the cold wall,  $\theta^{(11)}(\eta = 1) = -H x^{(11)}(\eta = 1)$ . Using equation 88 to determine  $x^{(11)}(\eta = 0)$  and  $x^{(11)}(\eta = 1)$ , equation 99 becomes:

$$E^{(11)} = - \frac{H\alpha^2}{16} \left( \frac{\beta}{E^{(0)}} \right) \frac{[1 - (1-E^{(0)})^{3-m+6\beta/E^{(0)}}]}{(3-m+6\beta/E^{(0)})} \\ - \frac{H\alpha\beta}{8} \left( 1 + \frac{\beta}{E^{(0)}} \right) \frac{[1 - (1-E^{(0)})^{2-m+6\beta/E^{(0)}}]}{(2-m+6\beta/E^{(0)})} . \quad (100)$$

This result shows that with catalytic walls, as the gas departs from local equilibrium, there is a change in the dimensionless energy transport variable only in the presence of a pressure gradient. This is what would be expected, because it was found that the dimensionless energy transport variable with catalytic walls is the same (to  $O(\epsilon)$ ) whether the flow is frozen or in equilibrium, if there is no pressure gradient.

#### Non-Catalytic Walls

In this case, the diffusion flux  $\Gamma$  vanishes at both walls. The composition cannot be in equilibrium in the neighborhood of the walls, even to  $O(\epsilon)$ , because this is incompatible with the boundary condition. For example, the equilibrium composition given by equation 87 leads to the non-zero diffusion flux of equation 90. These equations are valid in the main stream, but in obtaining equation 87, derivatives have been neglected which become important near the boundaries. That the solution has a true boundary layer character, i. e. that equation 87 is valid in the main stream regardless of the boundary conditions if  $\xi \ll 1$ , can be demonstrated by an argument which parallels that given for catalytic walls (after equation 94); it need not be repeated here. The boundary layer effect is more important with non-catalytic walls, however, because the singular perturbation occurs in  $O(\epsilon)$  terms rather than  $O(\epsilon\xi)$  terms.

New independent variables are appropriate in the boundary layers, as before:

$$\begin{aligned} z &= \eta / \xi^{\frac{1}{2}} & (\text{hot wall, } \eta \longrightarrow 0) \\ z &= 1 - \eta / \xi^{\frac{1}{2}} & (\text{cold wall, } \eta \longrightarrow 1) \end{aligned}$$

From equations 46 and 85:

$$\frac{d^2 x^{(10)}}{dz^2} = 2 \left[ (x^{(10)})^2 \frac{\pi}{\theta^{(0)}} - e^{-\alpha \eta} \right] \left( \frac{\pi}{\theta^{(0)}} \right)^2 (\theta^{(0)})^m. \quad (101)$$

The vanishing of the diffusion flux at the wall puts a condition on the concentration gradient, but there is no reason to expect that the concentration itself will depart strongly from local equilibrium. This leads to the assumption:

$$x^{(10)} = x_e^{(10)} + y = \left( -\frac{\theta^{(0)}}{\pi} \right)^{\frac{1}{2}} e^{-\frac{\alpha \eta}{2}} + y$$

where  $x_e^{(10)}$  is the local equilibrium value as shown, and  $y \ll x_e^{(10)}$ .

With this substitution, equation 101 can be linearized, noting that

$$d^2 x_e^{(10)} / dz^2 = O(\xi):$$

$$\frac{d^2 y}{dz^2} = \left[ 4 \left( \frac{\pi}{\theta^{(0)}} \right)^{5/2} (\theta^{(0)})^m e^{-\frac{\alpha \eta}{2}} \right] y = C_1 y$$

where  $C_1$  can be treated as a constant in the boundary layer (to  $O(\xi)$ ) and is evaluated at  $\eta = 0$  or  $\eta = 1$ , depending on which boundary layer is being considered. The solution is:

$$y = A e^{-\sqrt{C_1} z} + B e^{+\sqrt{C_1} z}. \quad (102)$$

One boundary condition is:

$$z \longrightarrow \infty; \quad y \longrightarrow 0.$$

Therefore  $B = 0$ . The remaining boundary condition is given by the dif-



fusion equation:

$$\begin{aligned}\Gamma^{(10)} &= -\frac{dx_e^{(10)}}{d\eta} - \frac{\beta x_e^{(10)}}{1-E^{(0)}\eta} - \frac{dy}{d\eta} - \frac{\beta y}{1-E^{(0)}\eta} \\ &= \Gamma_e^{(10)} - \frac{dy}{d\eta} - \frac{\beta y}{1-E^{(0)}\eta}\end{aligned}$$

where

$$\Gamma_e^{(10)} = \frac{1}{2}(\alpha + \frac{E^{(0)}}{1-E^{(0)}\eta}) e^{-\frac{\alpha\eta}{2}} (1-E^{(0)}\eta)^{\frac{1}{2}} + \beta/E^{(0)} \quad (\text{see equation 90}).$$

From equation 102:

$$\frac{dy}{d\eta} = -\frac{A \sqrt{C_1}}{\xi^{\frac{1}{2}}} e^{-\sqrt{C_1} z}.$$

Therefore, from the boundary condition  $\Gamma^{(10)} = 0$  at  $\eta = 0$  (where  $C_1 = 4$ ):

$$A = -\frac{\xi^{\frac{1}{2}}(\alpha + E^{(0)})}{2(2 - \xi^{\frac{1}{2}}\beta)} \approx -\xi^{\frac{1}{2}} \frac{(\alpha + E^{(0)})}{4}.$$

Then in the boundary layer at the hot wall,

$$x^{(10)} = x_e^{(10)}(0) + y = 1 - \frac{\xi^{\frac{1}{2}}(\alpha + E^{(0)})}{4} e^{-2\eta/\xi^{\frac{1}{2}}}. \quad (103)$$

Since  $y/x_e^{(10)} = O(\xi^{\frac{1}{2}})$ , the linearization of equation 101 is justified.

Similarly, in the boundary layer at the cold wall,

$$x^{(10)} = (1-E^{(0)})^{\frac{1}{2}} + \beta/E^{(0)} e^{-\frac{\alpha}{2}} \left[ 1 + \frac{\xi^{\frac{1}{2}}}{2\sqrt{C}} (\alpha + \frac{E^{(0)}}{1-E^{(0)}}) e^{-2(1-\eta)/\xi^{\frac{1}{2}}} \right] \quad (104)$$

where

$$C = 4(1-E^{(0)})^{m-\frac{5}{2}} - 5\beta/E^{(0)} e^{-\frac{\alpha}{2}}.$$

In the main stream the temperature distribution is given by equation 91.

However, the boundary conditions  $\theta^{(10)}(\eta = 0)$  and  $\theta^{(10)}(\eta = 1)$  are to

be found by integrating the energy equation through the boundary layers.  
As before, in the boundary layers:

$$\frac{d\theta^{(10)}}{dz} + H \frac{dx^{(10)}}{dz} = 0.$$

Since  $\theta^{(10)}(0) = 0$  and at the hot wall  $x^{(10)}$  is given by equation 103:

$$\begin{aligned} \theta^{(10)} &= -H \left[ x^{(10)} - x_e^{(10)}(z=0) \right] = -\frac{H\xi^{\frac{1}{2}}}{4} (\alpha + E^{(0)})(1 - e^{-2z}) \\ \theta^{(10)}(\eta \rightarrow 0) &= \theta^{(10)}(z \rightarrow \infty) = -\frac{H\xi^{\frac{1}{2}}}{4} (\alpha + E^{(0)}) \end{aligned} \quad (105)$$

Similarly, at the cold wall

$$\theta^{(10)}(\eta \rightarrow 1) = \frac{H\xi^{\frac{1}{2}}}{2\sqrt{C}} (1 - E^{(0)})^{\frac{1}{2} + \beta/E^{(0)}} e^{-\frac{\alpha}{2}} \left( \alpha + \frac{E^{(0)}}{1 - E^{(0)}} \right)$$

where

$$C = 4(1 - E^{(0)})^m - \frac{5}{2} - 5\beta/E^{(0)} e^{-\frac{\alpha}{2}}.$$

The energy transport is then given by:

$$\begin{aligned} E^{(10)} &= H \left\{ 1 - e^{-\frac{\alpha}{2}} (1 - E^{(0)})^{\frac{1}{2} + \beta/E^{(0)}} - \frac{2\beta}{\alpha} \left[ 1 - e^{-\frac{\alpha}{2}} (1 - E^{(0)})^{-\frac{1}{2} + \beta/E^{(0)}} \right] \right. \\ &\quad \left. - \frac{\xi^{\frac{1}{2}}}{4} \left[ \alpha + E^{(0)} - \left( \alpha + \frac{E^{(0)}}{1 - E^{(0)}} \right) e^{-\frac{\alpha}{4}} (1 - E^{(0)})^{\frac{1}{2}(\frac{7}{2} - m + 7\beta/E^{(0)})} \right] \right\} \end{aligned} \quad (106)$$

The  $O(\epsilon\xi)$  energy transport term is given by equation 99, with the boundary conditions again obtained by integrating the energy equation through the boundary layer. The procedure is the same as that which led to the  $O(\epsilon\xi^{\frac{1}{2}})$  term in equation 106, but in this case it leads to an  $O(\epsilon\xi^{3/2})$  term. To be consistent with the previous calculations, which have been carried only to  $O(\epsilon\xi)$ , this term will not be included here. Consequently,

$$E^{(11)} = H \left\{ \frac{\alpha^2}{16} \frac{(3-m+5\beta/E^{(0)})}{(3-m+6\beta/E^{(0)})} \left[ 1 - (1-E^{(0)})^{3-m+6\beta/E^{(0)}} \right] \right. \\ \left. + \frac{\alpha E^{(0)}}{8} \frac{[2-m+(7-m)\beta/E^{(0)}+5(\beta/E^{(0)})^2]}{(2-m+6\beta/E^{(0)})} \left[ 1 - (1-E^{(0)})^{2-m+6\beta/E^{(0)}} \right] \right\} \quad (107)$$

### A Numerical Example: Bromine Dissociation

To illustrate the near-equilibrium case, a numerical example has been calculated for the pure bromine dissociation. Although the near-equilibrium state usually corresponds to pressures and temperatures different from those for a frozen flow (since the rate parameter  $R$  is proportional to  $p^3$ , for example), the boundary conditions used here are exactly the same as for the frozen flow example represented in figures 1 and 2;  $p_0 = 1$  atmosphere,  $T_0 = 1500^\circ K$ , and  $E^{(0)} = 0.25$ . This permits a direct comparison of the near-frozen case and the near-equilibrium case.

Figure 5 shows the energy transport to  $O(\epsilon)$ . This corresponds to infinite reaction rates ( $\xi = 0$ ). If the reaction rate is so large that  $\xi$  is completely negligible, the energy transport is given by figure 5 independently of the degree of catalytic action provided by the wall surfaces. Reaction boundary layers at the walls may be of the order of 10 mean free paths or less in thickness, under these circumstances. As a result, the temperature itself does not change appreciably through the boundary layer, even though the temperature gradient at the wall may be quite steep, particularly if the diffusion flux vanishes at the wall and all energy transport there is by conduction. It follows that when reaction rates are extremely high the main stream "sees" essentially the temperature and pressure of the wall as boundary conditions, regardless of the boundary

layer, and is therefore independent of the catalytic nature of the wall. In treating the oxygen dissociation example, Hirschfelder (5) does not consider rate effects, but he points out that the chemical profile and heat transfer are practically independent of the boundary conditions on the diffusion flux. The conditions he chose for his example correspond to  $\xi \sim 10^{-6}$ , and according to figures 6 and 7, which give the correction on figure 5 due to finite rates, his conclusion is valid even for much larger values of  $\xi$ .

Figure 5 shows that the energy transport depends quite strongly on  $\beta$  in equilibrium flow; in fact, the dependence is nearly as great as in frozen flow with catalytic walls, figure 1. However, the explanation is different. In frozen flow, the effect is traceable to pressure diffusion alone. Here, it is due primarily to the shift in equilibrium caused by changes in the local pressure. As equation 89 shows, the diffusion flux depends on the local concentration. As the pressure increases the concentration of atoms decreases, because the recombination reaction is strengthened by the greater frequency of three-body collisions; the diffusion flux then decreases, reducing the contribution of diffusion to the energy transport.

This pressure gradient effect is particularly strong in the bromine example, however, because the activation energy for bromine dissociation is relatively small. As equation 92 shows, the smaller this activation energy ( $\alpha = \theta_a E^{(0)}$ ) the greater the importance of the term proportional to  $\beta$ . For example, with oxygen, which has a dissociation activation energy roughly three times that of bromine, the pressure gradient effect would be reduced by a factor of about three.\*

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\* It should also be noted that with a larger value for  $\theta_a$ , much higher wall temperatures are required to achieve an equivalent degree of dissociation. See the definition of  $\epsilon$ , equation 53.

As has already been mentioned, with catalytic walls the energy transport is the same (to  $O(\epsilon)$ ) whether the flow is frozen or in equilibrium, as long as  $\beta = 0$ . Therefore, the absence of a first-order rate effect as the flow departs from equilibrium with  $\beta = 0$ , as shown in figure 6, is expected. When there is a pressure gradient, the energy transport decreases as the gas departs from equilibrium. This again is primarily an indirect effect, due to the influence of pressure on the local composition. It is the inverse of the effect described in connection with a departure from frozen flow. When the gas departs from equilibrium the dissociation reaction predominates, and the greater the pressure the more frequent the reactions. With a pressure gradient the pressure is highest near the cold wall, and hence the increase in atom concentration is highest there. This tends to reduce the concentration gradient and therefore the diffusion flux of energy.

The rate effect with non-catalytic walls is given by figure 7. It is a much stronger effect than that with catalytic walls, because there is an  $O(\epsilon^{\frac{1}{2}})$  term (given by  $\psi_3$ ) as well as an  $O(\epsilon\xi)$  term (given by  $\psi_4$ ). As the mixture departs from equilibrium, the energy transport decreases because the transport by diffusion is diminished. (In the limiting case of frozen flow, the diffusion vanishes for these boundary conditions.) The pressure gradient enhances this effect through the influence of pressure on reaction rate, as already explained in connection with catalytic walls.

## VI. SUMMARY: THE BINARY DISSOCIATING GAS

In the previous two sections the energy transport behavior of the two-component reacting gas has been considered when the gas is nearly chemically frozen and when it is nearly in local chemical equilibrium. The numerical examples for bromine dissociation show the effects of a pressure gradient and of varying rates within these opposite realms. However, the individual curves presented for frozen and equilibrium flow do not provide any easily interpreted picture of the nature of the solution throughout the reaction-rate regime. Of course, the very basis of the perturbation technique makes it impossible to give an accurate description of the behavior when the chemical reaction rate is neither large nor small relative to the diffusion rate, but it is possible to obtain some notion of the general character of the overall solution.

For this purpose, it is convenient to display the results of the bromine dissociation calculation with a linear scale for the dimensionless energy transport and a logarithmic scale for the ratio (reaction rate/diffusion rate). This makes it possible to include the entire rate spectrum on one graph. The chief disadvantage is that the logarithmic scale tends to distort the curves somewhat.

Figure 8 shows the calculated results for bromine dissociation with perfectly catalytic walls and three different pressure gradients. The solid curves correspond to the solutions given by the perturbation technique of the previous sections. When there is no pressure gradient ( $\beta = 0$ ), the total energy transport in either completely frozen or completely equilibrium flow is exactly the same. Furthermore, the perturbation solutions show no first-order rate effects in either case. Conse-

quently, it seems reasonable to expect that the dimensionless energy transport is constant in the absence of a pressure gradient, independently of the chemical regime, and the solid curves are joined by a dashed line.

It should be noted that the same pressure and temperature boundary conditions,  $p_0$  and  $T_0$ , were used throughout the calculations. This provides solutions for near-frozen and near-equilibrium flow which can be compared simply and directly, as in figure 8. However, it also means that changes in the reaction rate parameter plotted along the abscissa must be accomplished by varying the physical dimensions of the system, specifically the channel width  $w$ . Therefore, although the dimensionless energy transport variable remains constant when  $\beta = 0$ , the actual energy flux  $Q$  (units: energy/time/area) decreases as the chemical regime changes from frozen to chemical equilibrium flow with the pressure and temperature boundary conditions held fixed.

The remaining curves of figure 8 show the effects of a pressure gradient when the walls are catalytic. In either completely frozen or completely equilibrium flow, an increasing pressure gradient reduces the energy transport (when the pressure gradient and temperature gradient are opposite in direction.) The explanation for this reduction is quite different in the two cases; although the effect is approximately of the same magnitude for frozen or equilibrium flow in the bromine association example, this is not necessarily true in general. In frozen flow the energy transport decreases with increasing pressure gradient because of pressure diffusion alone. In equilibrium flow the ultimate effect is similar, but the cause is more complicated and less direct. Because the local recombination rate depends on the local density, and therefore the local pressure, changes in the pressure gradient influence the concentration

distribution. This in turn changes the concentration diffusion flux, and thus the energy transport. In equilibrium flow the size of the pressure gradient effect depends on the activation energy of the reaction, which is not surprising in view of the mechanism just described.

Figure 8 also indicates that if there is a pressure gradient, the dimensionless energy transport has a minimum somewhere in the region where the gas is neither frozen nor in equilibrium. The perturbation technique provides no basis for a reasonable estimate of the character of the solution in this region. The minimum is apparently absent when  $\beta = 0$ , and the curves suggest that it becomes more pronounced as the pressure gradient increases.

The corresponding curves for non-catalytic walls are shown in figure 9. When the gas is completely chemically frozen, the diffusion flux must vanish everywhere if it vanishes at the walls, to satisfy the continuity equation. Therefore, the energy transport is entirely due to ordinary heat conduction, and there is no pressure gradient effect, of course. As the gas "unfreezes" a diffusion flux can occur except at the walls, and this accounts for the indicated rise in the energy transport.

At the other extreme of the rate parameter scale, where the gas is in chemical equilibrium, the situation is very similar to that just described for catalytic walls. In fact, the concentration and temperature profiles are identical in the two cases, except in the thin reaction boundary layers near the walls. The non-catalytic influence of the walls is confined within these boundary layers, which remain extremely thin relative to the channel width when the ratio (reaction rate/diffusion rate) is very large. As was shown in the preceding section, under such condi-



tions the solution has a true boundary-layer character, in that it is essentially independent of the catalytic nature of the walls. Accordingly, a comparison of figures 8 and 9 shows that as the gas nears a state of local chemical equilibrium, the energy transport (for a given  $\beta$ ) approaches the same value whether the walls are catalytic or non-catalytic. As the gas leaves the equilibrium state, a much stronger reduction in energy transport is felt with non-catalytic walls than with catalytic walls. The boundary layers grow rapidly, carrying the non-catalytic influence of the walls into the main stream and reducing the diffusion flux. Ultimately, when the gas is frozen, the wall influence dominates everywhere; there is no diffusion flux and therefore no diffusive energy transport. It seems reasonable to expect that the solution will have a smooth, continuous behavior, and on this assumption, the solid curves obtained with the perturbation technique have been joined by dashed curves.

One of the most interesting features of the binary reacting gas is the fact that the order of the governing system of equations is reduced when the gas is in local chemical equilibrium. It is shown in Appendix A that the equations for the two-component gas in equilibrium can always be made formally identical with the corresponding equations for a single-component gas. The effects of diffusion in the former are accounted for by an "effective thermal conductivity". Thus, the order of the set of equations for a binary reacting gas in local equilibrium is the same as for a single-component gas. This is true only when the gas is in local chemical equilibrium, and it is this property which leads to the reaction boundary layers characteristic of the equilibrium solution.

In the following section a gas composed of three species, with the

reacting components in equilibrium, is investigated within the framework of the channel-flow approximation already used. The primary purpose is to show in what respects the gas of three (or more) components in local chemical equilibrium may be similar to, or different from, the binary gas in equilibrium.

## VII. THE THREE-COMPONENT GAS IN LOCAL CHEMICAL EQUILIBRIUM

The treatment of the binary reacting gas in the preceding sections has shown that the character of the chemically frozen flow is quite different from that of the flow which is in local chemical equilibrium. When the mixture is frozen, the order of the system of equations is two higher than for a single, non-reacting gas; this is due to the addition of a diffusion equation and a continuity equation to the other conservation equations of the set. The higher order is necessary and sufficient to satisfy boundary conditions which physically correspond to specification of the catalytic nature of the walls. Consequently, the energy transport is strongly coupled to the catalytic influence of the wall surfaces. The extension of the analysis to include the general multi-component, chemically frozen gas is apparently straightforward in principle, although the complexity of the calculation grows rapidly as the total number of components involved in the gas increases. With the addition of each component the order of the set of equations will be raised by two, and so will the number of boundary conditions to be satisfied. If more than one chemical element is present in the gas, as will usually be the case when the mixture includes three or more chemical species, the boundary conditions to be satisfied by the mole fractions will depend not only on the catalytic nature of the walls, but also on the total mass of each of the various chemical elements initially introduced into the system. In other words, when more than one chemical element is present in the chemically frozen gas mixture, the energy transport will depend on the proportions of the various elements in the system and also on the catalytic action of the wall surfaces. The de-

pendence on initially-present proportions of various elements does not appear in the frozen-flow solution for the simple binary dissociation reaction, because only one element is present.

On the other hand, it is shown in Appendix A that when the binary gas is in local chemical equilibrium, the order of the system of equations is the same as for a single-component gas. This feature leads to the reaction boundary layers characteristic of the equilibrium flow. In the immediate vicinity of the walls the catalytic action of the surfaces may cause reaction rates to become important, effectively raising the order of the set of equations by two. This is the mechanism by which the necessary boundary conditions on the mole fractions are satisfied. The boundary layers "shield" the main stream from the catalytic action of the walls, so that the temperature and composition profiles in the main body of the gas, and the energy transport, are practically independent of the chemical influence of the boundary surfaces.

Hirschfelder (5) has indicated that an effective coefficient of thermal conductivity can be defined not only for the binary gas, but for the multi-component mixture in general, as long as the gas is in a state of local chemical equilibrium. This implies that the order of the set of equations for a general, multi-component gas in chemical equilibrium is the same as for a simple, single-component gas. Under these circumstances the solution for any number of components would clearly have a boundary layer character similar to that of the binary gas, for the main-stream solution would be completely determined when boundary conditions on the pressure and temperature were specified. It would also follow that the profiles in the main stream, and the energy transport, are essentially

independent of the proportions of the various chemical elements initially present in the system, just as in the binary example where only one element was present. These mass proportions must in some way affect the mole fractions of the various species, presumably by providing the information which, together with specification of the catalytic nature of the walls, will determine the boundary conditions on the various mole fractions. However, if the main-stream mole-fraction profiles are completely determined by the pressure and temperature boundary conditions, then the influence of the initially introduced mass proportions of various elements, as well as rate effects, must be confined to the boundary layers.

It is not too difficult to anticipate that the multi-component gas in equilibrium will have a behavior which is practically independent of the catalytic nature of the walls, with rate effects and the wall influence restricted to thin reaction boundary layers, as in the binary case. If the boundary surface retards the reaction, for example, forcing the composition away from local equilibrium, and if the reactions in the gas are very fast compared with the rates of diffusion processes, the composition should reach local chemical equilibrium within a few mean-free-paths of the wall. This will occur in a very narrow region relative to the characteristic length of the system, regardless of how much the composition deviates from equilibrium at the wall; the ratio (reaction rate/diffusion rate)  $\gg 1$  ensures this. Thus the solution is practically independent of the chemical action of the walls, whose influence on the rates is confined to very thin regions near the boundaries. This crude physical argument seems to apply equally well to any number of reacting components.

On the other hand, it seems intuitively unreasonable that the energy transport and composition profiles should be essentially independent of the masses of various elements originally introduced into the system. In fact, this cannot be true. Large changes in the proportions of elements involved in the reaction must ultimately result in extensive changes in the total amount of each of the components (composed of these elements) which will finally be present when local equilibrium is reached; this is required to conserve mass. This means that the various mole fractions must be strongly influenced by the proportions of various chemical elements present, and furthermore, that this influence is not restricted to boundary layers. By definition, the boundary layers are thin and contain only a small fraction of the total mass in the system. Large changes in the mole fractions within the boundary layers alone would not appreciably alter the total proportion of each constituent present, and therefore could not answer the requirements of large changes in the proportions of various chemical elements present.

The addition of each component beyond two does, in fact, raise the order of the set of governing equations by two. This precludes the possibility of defining a generalized coefficient of thermal conductivity and describing the flow with a formalism similar to that for a simple, single-component gas, except in the special case of a binary mixture in local chemical equilibrium.

The solution given by this set of equations corresponds to the main stream, and the extra constants made available by the higher order of the set are necessary and sufficient to ensure that mass is conserved. In this way the solution becomes strongly coupled with the proportions of elements introduced into the system, as expected intuitively. With any num-

ber of reacting species in equilibrium, rate effects are confined to the reaction boundary layers, just as in the binary case, and the behavior is practically independent of the catalytic nature of the walls.

Because the equations acquire an immense complexity when many components are present, it is hardly feasible, even if desirable, to demonstrate the character of the multi-component, equilibrium flow in a general way. However, the features which have just been described can be illustrated by means of two simple examples involving three components and analogous to the channel-flow perturbation analyses of the two-component dissociation reaction. At the same time, these examples show how the three-component gas may differ from the binary case with regard to the dependence of energy transport on the pressure gradient.

#### The Three-Component Gas in the Channel-Flow Approximation

The physical significance of the channel-flow approximation has been explained in Section III and requires no further discussion here. The primary difference between the equations presented there for the binary mixture and those for the three-component gas is that an additional diffusion equation and an additional continuity equation (or stoichiometry relation) are required in the latter case. The problem can be formulated in terms of the mole fractions and diffusion velocities of species 1 and 2 alone, eliminating the mole fraction of species 3 with the equation

$$x_1 + x_2 + x_3 = 1 \quad (108)$$

and eliminating the diffusion velocity  $u_3$  through the following relation, which stems from equation 4:

$$n_1 m_1 u_1 + n_2 m_2 u_2 + n_3 m_3 u_3 = 0 \quad (109)$$

The equation of motion is independent of the number of components:

$$\frac{d \ln \pi}{d\eta} = \frac{2\beta}{1 - E^{(0)}\eta} \quad (110)$$

The symbols have already been defined in connection with equation 38, and these definitions are unchanged.

The energy equation reduces to:

$$- \frac{d\theta}{d\eta} + H_{13} \Gamma_1 + H_{23} \Gamma_2 = E \quad (111)$$

where

$$\theta = T/T_o$$

$$\Gamma_1 = n_1 u_1 / n D_{12}$$

$$\Gamma_2 = n_2 u_2 / n D_{12}$$

$$H_{13} = (h_1 - m_1/m_3 h_3) Le / \bar{C}_p T_o$$

$$H_{23} = (h_2 - m_2/m_3 h_3) Le / \bar{C}_p T_o$$

$E$  = total dimensionless energy transport = constant.

The appropriate diffusion equations may be obtained from equations 11 and 12. They are:

$$\begin{aligned} x_1 \Gamma_2 - x_2 \Gamma_1 - \frac{a_1}{\mu} x_1 \Gamma_1 - \frac{m_2}{m_3} a_1 x_1 \Gamma_2 - a_1 (1 - x_1 - x_2) \Gamma_1 \\ = \frac{dx_1}{d\eta} + x_1 \left\{ \frac{(\mu - 1) \left[ 1 - x_1 - \left( \frac{\mu - m_2/m_1}{\mu - 1} \right) x_2 \right]}{\mu \left[ 1 - \left( \frac{\mu - 1}{\mu} \right) x_1 - \left( \frac{\mu - m_2/m_1}{\mu} \right) x_2 \right]} \right\} \frac{d \ln \pi}{d\eta} \end{aligned} \quad (112)$$

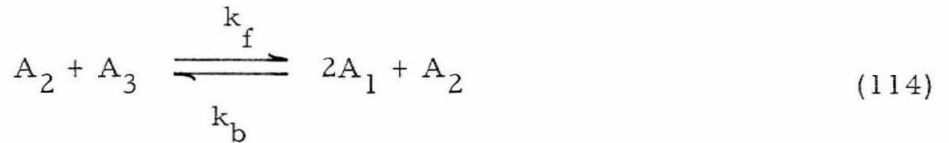


$$\begin{aligned}
 x_2 \Gamma_1 - x_1 \Gamma_2 - \frac{1}{a_3} \frac{m_2}{m_3} x_2 \Gamma_2 - \frac{a_1}{a_2 \mu} x_2 \Gamma_1 - \frac{(1-x_1-x_2) \Gamma_2}{a_3} \\
 = \frac{dx_2}{d\eta} + x_2 \left\{ \frac{(\mu - \frac{m_2}{m_1}) \left[ 1 - x_2 - (\frac{\mu - 1}{\mu - m_2/m_1}) x_1 \right]}{\mu \left[ 1 - (\frac{\mu - 1}{\mu}) x_1 - (\frac{\mu - m_2/m_1}{\mu}) x_2 \right]} \right\} \frac{d \ln \pi}{d\eta} \quad (113)
 \end{aligned}$$

where

$$a_1 = \frac{D_{12}}{D_{13}} ; a_2 = \frac{D_{23}}{D_{13}} ; a_3 = \frac{D_{23}}{D_{12}} ; \mu = \frac{m_3}{m_1} .$$

The form of the chemical equilibrium relation depends on the specific reaction being considered. The simplest reaction involving three components, and one of the two which will be considered here, is the binary dissociation reaction in the presence of a third, inert species, e. g. bromine dissociation in the presence of argon. Such a reaction can be represented symbolically by:



When the composition is in chemical equilibrium:

$$\frac{K_n}{n_o} \left( \frac{\theta}{\pi} \right) = \frac{x_1^2}{1 - x_1 - x_2} \quad (115)$$

where  $K_n$  is the equilibrium constant, and  $n_o$  is the total concentration at  $\eta = 0$ .

The addition of a third species also adds a new continuity equation to the set. This equation follows from equation 5. Since  $A_2$  is inert in the reaction of equation 114, the production rate  $K_2$  in equation 5 van-

ishes, and if  $nD_{12}$  is treated as a constant as before,

$$\nabla \cdot \Gamma_2 = 0 .$$

In the channel-flow approximation  $\Gamma_2$  is a function of  $\eta$  alone; therefore, the continuity equation can be integrated at once to yield (for the reaction of equation 114) :

$$\Gamma_2 = \text{constant} . \quad (116)$$

The second example of a three-component reaction to be considered here can be represented symbolically by the expression:



When this reaction has achieved local chemical equilibrium, the mole fractions will be related through the equilibrium constant:

$$K_n = \frac{(1 - x_1 - x_2)^2}{x_1 x_2} . \quad (118)$$

In addition, a continuity equation is required. For this example, it is convenient to use a stoichiometry relation which arises from the reaction of equation 117 and corresponds to a linear combination of two continuity equations. It follows from equation 117 that for every mole of  $A_1$  produced locally by the dissociation of  $A_3$ , a mole of  $A_2$  is also created. This leads to the equation:

$$\nabla \cdot (n_1 u_1 m_1) = \nabla \cdot (n_2 u_2 m_2) .$$

Dividing by  $nD_{12}$ , which is treated as a constant, this can be integrated at once to obtain:

$$\Gamma_1 - \frac{m_2}{m_1} \Gamma_2 = C' \quad (\text{constant}) \quad (119)$$

Using the equations just presented, a perturbation technique similar to that of the binary analysis can now be used to study the reactions of equations 114 and 117, in an effort to demonstrate some of the features of the three-component flow and the multi-component gas in general.

### The Chemical Equilibrium Flow of Two Reacting Components in the Presence of an Inert Species

In this case, the reaction to be considered is given by equation 114. When the mass of the inert component  $A_2$  originally introduced into the system vanishes, the solution must reduce to that previously obtained in the binary chemical equilibrium analysis for  $\xi = 0$  (infinite reaction rate), because the reaction then becomes the binary dissociation studied there.

In the present analysis the dependent variables and energy transport eigenvalue (total energy transport  $E$  of the energy equation) are expressed as follows:

$$\begin{aligned}
 \theta &= \theta^{(0)} + \nu \theta^{(01)} + \dots + \epsilon(\theta^{(10)} + \nu \theta^{(11)} + \dots) + O(\epsilon^2) + O(\nu^2) \\
 x_1 &= 0 + 0 + \dots + \epsilon(x^{(10)} + \nu x^{(11)} + \dots) + O(\epsilon^2) \\
 \Gamma_1 &= 0 + 0 + \dots + \epsilon(\Gamma_1^{(10)} + \nu \Gamma_1^{(11)} + \dots) + O(\epsilon^2) \\
 x_2 &= 0 + \nu x_2^{(01)} + \dots + \epsilon(0 + \nu x_2^{(11)} + \dots) + O(\nu^2) \\
 \Gamma_2 &= 0 + \nu \Gamma_2^{(01)} + \dots + \epsilon(0 + \nu \Gamma_2^{(11)} + \dots) + O(\nu^2) \\
 E &= E^{(0)} + \nu E^{(01)} + \dots + \epsilon(E^{(10)} + \nu E^{(11)} + \dots) + O(\epsilon^2) + O(\nu^2)
 \end{aligned} \tag{120}$$

The expansion parameter  $\epsilon$  is defined exactly as before, i. e. by equation 53, and  $K_n/n_o$  is approximated by an expression similar to equation 55:

$$\frac{K_n}{n_o} = \epsilon^2 e^{-\alpha\eta} \left[ 1 + \nu \frac{\theta_a \theta^{(01)}}{(\theta^{(o)})^2} + \epsilon \frac{\theta_a \theta^{(10)}}{(\theta^{(o)})^2} + \dots \right] \quad (121)$$

The purpose of the second expansion parameter  $\nu$  is to conveniently introduce another restriction into the formalism. The mole fraction of the inert species will be assumed to be small, i.e.  $x_2 \ll 1$ . This can be accomplished by restricting the total mass of  $A_2$  initially injected into the system to some small fraction of the total mass of reacting components, which leads to a definition for  $\nu$ . It will be assumed arbitrarily that  $x_2^{(01)}(\eta = 0) = 1$ ,  $x_2^{(11)}(\eta = 0) = 0$ , etc. Then  $\nu$  is determined by the equation:

$$M_{A_2} = \nu m_{A_2} \int_0^1 x_2 n(\eta) d\eta = \nu m_{A_2} \int_0^1 x_2 \frac{p_o}{R T_o} \frac{\pi(\eta)}{\theta(\eta)} d\eta \quad (122)$$

where  $M_{A_2}$  is the mass per unit volume of  $A_2$  in the system, and  $m_{A_2}$  is the molecular weight of  $A_2$ .

As before, the zeroth-order energy equation corresponds to ordinary heat conduction in a single-component gas:

$$- \frac{d\theta^{(o)}}{d\eta} = E^{(o)} \quad (123)$$

The solution is:

$$\theta^{(o)} = 1 - E^{(o)}\eta \quad (124)$$

The  $O(\nu)$  energy equation is:

$$- \frac{d\theta^{(01)}}{d\eta} + H_{23} \Gamma_2^{(01)} = E^{(01)} \quad (125)$$

According to equation 116, which is the continuity equation for the inert species,  $\Gamma_2 = \text{constant}$ . Since  $A_2$  is inert, molecules of this species cannot undergo a chemical reaction at the walls, regardless of the catalytic

nature of the surfaces. The diffusion flux  $\Gamma_2$  therefore vanishes at the walls, and consequently:

$$\Gamma_2 = \Gamma_2^{(01)} = \Gamma_2^{(11)} = \dots = \Gamma_2^{(mn)} = 0 \text{ (everywhere)} \quad (126)$$

Equation 125 can be integrated at once, and since equation 124 satisfies the boundary conditions on the temperature, it follows that  $\theta^{(01)}(0) = \theta^{(01)}(1) = 0$  and

$$E^{(01)} = 0 . \quad (127)$$

When the solution is carried only to  $O(\epsilon)$ , it gives the first-order effect when the binary dissociation takes place in the absence of any other gas ( $\nu = 0$ ). To this order, the problem is therefore identical with that solved in Section V. From this, it can be anticipated that  $x_1^{(10)}$ ,  $\Gamma_1^{(10)}$ ,  $\theta^{(10)}$ , and  $E^{(10)}$  are given by the corresponding solutions obtained in that analysis, equations 87, 90, 91 and 92, respectively. Substitution of the expansions of equation 120 into equations 111, 112, 113 and 115 (with  $K_n/n_o$  given by 121) does, in fact, give for the  $O(\epsilon)$  terms exactly the formalism obtained in Section V, and this procedure will not be repeated here.

The effect of the inert component first appears in the  $O(\epsilon\nu)$  terms. Recalling that  $\Gamma_2^{(11)} = 0$ , the energy equation of this order is:

$$-\frac{d\theta^{(11)}}{d\eta} + H_{13} \Gamma_1^{(11)} = E^{(11)} . \quad (128)$$

To find  $\Gamma_1^{(11)}$ , so that this equation can be integrated and the leading effect of the inert species determined, it is necessary to turn to the equilibrium relation and diffusion equations. By equating the coefficients of  $O(\epsilon^2\nu)$  in equation 118, a relation between the mole fractions is obtained:

$$x_2^{(01)} = -2 x_1^{(11)}/x_1^{(10)} . \quad (129)$$

Assuming  $a_1 = a_2 = a_3 \approx 1$ , which has no essential influence on the character of the solution, equation 113 provides:

$$\frac{dx_2^{(01)}}{d\eta} + \left( \frac{\mu - m_2/m_1}{\mu} \right) x_2^{(01)} \frac{d \ln \pi}{d\eta} = - \Gamma_2^{(01)} = 0. \quad (130)$$

With the aid of equation 110, this expression can be integrated at once. When  $\nu$  was defined, it was arbitrarily assumed that  $x_2^{(01)}(0) = 1$ ; therefore:

$$x_2^{(01)} = (1 - E^{(0)}\eta)^{(\mu - m_2/m_1)2\beta/E^{(0)}/\mu} \quad (131)$$

The  $O(\epsilon\nu)$  terms of equation 112 give:

$$\begin{aligned} \Gamma_1^{(11)} = & - \frac{dx_1^{(11)}}{d\eta} - \left( \frac{\mu-1}{\mu} \right) x_1^{(11)} \frac{d \ln \pi}{d\eta} \\ & + \frac{1}{\mu^2} \left( \mu - \frac{m_2}{m_1} \right) x_1^{(10)} x_2^{(01)} \frac{d \ln \pi}{d\eta}. \end{aligned} \quad (132)$$

Equations 129 and 131 can be combined to give  $x_1^{(11)}$ . Then with the aid of equation 87 and equation 131,  $\Gamma_1^{(11)}$  can be obtained from 132:

$$\Gamma_1^{(11)} = - \left( \frac{\mu-1}{\mu^2} \right) \left( \alpha + \frac{E^{(0)}}{1-E^{(0)}\eta} \right) e^{-\frac{\alpha\eta}{2}} (1-E^{(0)})^{\frac{\mu-1}{\mu} + \left( \frac{2\mu-1-m_2/m_1}{\mu} \right) 2\beta/E^{(0)}} \quad (133)$$

When equation 133 is substituted into 128, the energy equation can be integrated to obtain:

$$\begin{aligned} \theta^{(11)} = & 2H_{13} \left( \frac{\mu-1}{\mu^2} \right) \left\{ 1 - \left( \frac{\mu-2}{\mu} \right) \frac{E^{(0)}}{\alpha(1-E^{(0)}\eta)} - \right. \\ & \left. \left( \frac{2\mu-1-m_2/m_1}{\mu} \right) \frac{4\beta}{\alpha(1-E^{(0)}\eta)} \right\} \cdot [\ ] = - E^{(11)}\eta + F^{(11)} \end{aligned} \quad (134)$$

where

$$[\ ] = e^{-\frac{\alpha\eta}{2}} (1-E^{(0)}) \frac{\mu-1}{\mu} + \left( \frac{2\mu-1-\frac{m_2}{m_1}}{\mu} \right) 2\beta/E^{(0)} .$$

The boundary conditions are  $\theta^{(11)}(0) = \theta^{(11)}(1) = 0$  . Therefore:

$$F^{(11)} = -2H_{13} \left( \frac{\mu-1}{\mu^2} \right) \left\{ 1 - \left( \frac{\mu-2}{\mu} \right) \frac{E^{(0)}}{\alpha} - \left( \frac{2\mu-1-\frac{m_2}{m_1}}{\mu} \right) \frac{4\beta}{\alpha} \right\} \quad (135)$$

and

$$E^{(11)} = -2H_{13} \left( \frac{\mu-1}{\mu^2} \right) \left[ 1 - e^{-\frac{\alpha}{2}} (1-E^{(0)}) \frac{\mu-1}{\mu} + \left( \frac{2\mu-1-\frac{m_2}{m_1}}{\mu} \right) 2\beta/E^{(0)} \right] \cdot \left\{ \right\} \quad (136)$$

where

$$\left\{ \right\} = \left\{ 1 - \frac{\left[ \left( \frac{\mu-2}{\mu} \right) E^{(0)} + \left( \frac{2\mu-1-\frac{m_2}{m_1}}{\mu} \right) 4\beta \right]}{\alpha} \right\} .$$

#### A Numerical Example: Bromine Dissociation in the Presence of Argon

To illustrate the effect of adding an inert component to the binary reacting gas, an example of bromine dissociation in the presence of argon has been calculated, and the results are presented in figure 10. The quantity  $\psi_5$  is equal to  $\epsilon E^{(11)}$ , with  $E^{(11)}$  obtained from equation 136 for the given temperature and pressure boundary conditions. It will be recalled that  $\nu$  is the mole fraction of the inert gas, in this case argon, at the hot wall ( $\eta = 0$ );  $\nu$  is determined when the total mass of argon and the total mass of bromine initially introduced into the system are specified. When no argon is present,  $\nu = 0$ , and the reaction reduces to the two-component bromine dissociation in local equilibrium, which was considered in Section V and illustrated by an example in figure 5. The pres-

sure and temperature boundary conditions used in obtaining figures 5 and 10 are identical. Consequently, these two figures can be used together to illustrate the influence of the presence of argon on the energy transport. When no argon is present, the energy transport is given by figure 5 alone; if the composition includes a small proportion of argon, there is an additional contribution  $\nu\psi_5$ , which can be obtained from figure 10.

Since the contribution of  $\psi_5$  is negative, the effect of an increasing proportion of the inert gas (with fixed temperature and pressure boundary conditions) is to reduce the energy transport. This is to be expected, because the inert species itself can make no contribution to the diffusive energy flux; the diffusion flux of the inert gas necessarily vanishes at the walls. The contribution of diffusion to the energy transport is due to the atomic bromine, which tends to form at the hot wall, diffuse to the cold wall, and there recombine, giving up its chemical heat of formation. The magnitude of this contribution depends on the mole fraction of atomic bromine (or really on the change in this mole fraction from the hot wall to the cold wall, which is a measure of the net extent of recombination of the atoms as they diffuse to the cold wall). As the mole fraction of argon increases, the mole fraction of bromine is proportionately reduced. This leads to a smaller contribution by the diffusion process to the energy transport.

The qualitative forms of the curves in figures 5 and 10 are the same. This can be anticipated, because figure 10 simply represents a reduction in the influence of the diffusion mechanism illustrated in figure 5. The slopes of the two curves are different, because the strength of the pressure-gradient effect depends on differences in the molecular weights



of the components involved, and the molecular weight of argon plays a role in figure 10, but not in figure 5.

This simple example shows that even the addition of an inert component to the binary reacting gas in equilibrium changes the mathematical formulation of the problem, raising the order of the set of equations by two. This does not alter the boundary-layer character of the solution with respect to the catalytic nature of the walls. Although no analysis of rate effects has been included in this example, it seems clear that such effects are confined to the reaction boundary layers, just as in the two-component case, and the treatment of these effects would parallel that given in connection with the binary problem.

When the third species is inert, the two additional constants provided by the higher order of the equations are determined by (a) the fact that the diffusion flux must vanish at the walls (and therefore everywhere, due to the continuity equation), and (b) the total masses of inert and reacting elements present in the system.

In a sense, the inert component is "uncoupled" from the reacting components. Its presence does not change the basic qualitative character of the problem. Instead, the inert component has the effect of "shifting" the solution corresponding to a binary reacting gas. When the composition includes an inert gas as well as two reacting ones, the total energy transport and the composition profiles of the reacting species behave almost as they would in a system containing only the reacting components, but with effective temperature and pressure boundary conditions different from those which are actually imposed. In other words, the addition of an inert species to a binary reacting gas in equilibrium, while holding the

temperature and pressure boundary conditions fixed, has nearly the same effect on energy transport and composition profile shapes as does adjusting the boundary conditions to provide a lower degree of dissociation in the original, pure, binary gas.

### The Chemical Equilibrium Flow of a Gas with Three Reacting Components

The second example involving three components is based upon the reaction of equation 117. The dependent variables and energy eigenvalue  $E$  are expressed by the following expansions:

$$\begin{aligned}
 \theta &= \theta^{(0)} + \epsilon \theta^{(1)} + \dots \\
 x_1 &= 0 + \epsilon x_1^{(1)} + \dots \\
 \Gamma_1 &= 0 + \epsilon \Gamma_1^{(1)} + \dots \\
 x_2 &= 0 + \epsilon x_2^{(1)} + \dots \\
 \Gamma_2 &= 0 + \epsilon \Gamma_2^{(1)} + \dots \\
 E &= E^{(0)} + \epsilon E^{(1)} + \dots
 \end{aligned} \tag{137}$$

The dimensionless expansion parameter  $\epsilon$  is defined very much as it has been in the previous perturbation analyses, and it corresponds to a restriction on the extent to which  $A_3$  dissociates into  $A_1$  and  $A_2$  in the gas. However, it is conventional to define the equilibrium constant for this reaction as in equation 118, and for most actual reactions which fit the scheme of equation 117 this means  $K_n$  decreases exponentially with increasing temperature, rather than increasing exponentially as before. Therefore, although the definition of  $\epsilon$  is similar to that of previous cases in principle, it is formally different. In the present example, the equilibrium constant can be represented by the equation:

$$K_n = C e^{+\theta_a/\theta} \tag{138}$$

As in the procedure leading to equations 53, 54 and 55, this provides the definition of  $\epsilon$  and the suitable approximate expression for  $K_n$  :

$$\epsilon = (C e^{+\theta_a} )^{-\frac{1}{2}} = (K_n(\eta = 0))^{-\frac{1}{2}} \quad (139)$$

$$\frac{1}{K_n} = \epsilon^2 e^{-\alpha\eta} \left[ 1 + \epsilon \frac{\theta_a \theta^{(1)}}{(\theta^{(0)})^2} + \dots \right] \quad (140)$$

where  $\alpha = \theta_a E^{(0)}$ .

The zeroth-order solution corresponds to a gas composed entirely of  $A_3$  and is given by the energy equation alone, as in the previous perturbation analyses:

$$\theta^{(0)} = 1 - E^{(0)}\eta \quad . \quad (141)$$

When the expansions of equation 137 are substituted into equation 112, again assuming  $a_1 = a_2 = a_3 \approx 1$ , the  $O(\epsilon)$  terms provide:

$$\Gamma_1^{(1)} = - \frac{dx_1^{(1)}}{d\eta} - \left( \frac{\mu-1}{\mu} \right) x_1^{(1)} \frac{2\beta}{1-E^{(0)}\eta} \quad (142)$$

Similarly, from equation 113:

$$\Gamma_2^{(1)} = - \frac{dx_2^{(1)}}{d\eta} - \left( \frac{\mu - \frac{m_2}{m_1}}{\mu} \right) x_2^{(1)} \frac{2\beta}{1-E^{(0)}\eta} \quad . \quad (143)$$

The mole fractions are related through the equilibrium constant. From equations 118, 137 and 140:

$$x_1^{(1)} x_2^{(1)} = e^{-\alpha\eta} \quad . \quad (144)$$

Also, from equation 119:

$$\Gamma_1^{(1)} - \frac{m_2}{m_1} \Gamma_2^{(1)} = C' \quad . \quad (145)$$

Equations 142, 143, 144 and 145 can be combined to yield a single differential equation in  $x_1^{(1)}$  (or  $x_2^{(1)}$ ). Unfortunately, this equation is non-linear, in general, due to the nature of equation 144. However, this difficulty can be overcome by noticing that if the reactant  $A_2$  has a low molecular weight while that of the other reactant is relatively large, then  $m_2/m_1$  may be negligibly small. This situation applies to an interesting group of reactions involving the halogens and hydrogen. For example, if  $A_2 = H_2$  and  $A_1 = Br_2$ , then  $m_2/m_1 = 1/80$ ; if  $A_1 = I_2$ , then  $m_2/m_1 = 1/127$ . It is entirely consistent with the perturbation treatment to neglect terms of this size. It follows from equation 145 that

$$\Gamma_1^{(1)} \approx C' \quad (146)$$

If the effect of changes in the molecular weight ratio  $m_2/m_1$  were of some particular interest, the problem could have been treated with a two-parameter perturbation technique, using  $m_2/m_1$  as the second expansion parameter. This would clearly have led to a result identical with equation 146. For present purposes it is sufficient to carry the solution only to  $O(\epsilon)$ , disregarding terms  $O(\epsilon m_2/m_1)$ . (No terms  $O(m_2/m_1)$  appear, because if  $\epsilon = 0$  there is no dissociation and therefore no diffusion.)

With the help of equations 146 and 110,  $x_1^{(1)}$  can be obtained easily from equation 142. The result is:

$$x_1^{(1)} = G (1 - E^{(0)} \eta) + F (1 - E^{(0)} \eta) \left( \frac{\mu - 1}{\mu} \right) 2\beta / E^{(0)} \quad (147)$$

where

$$G = \frac{C'}{E^{(0)} \left[ 1 - \left( \frac{\mu - 1}{\mu} \right) \frac{2\beta}{E^{(0)}} \right]} \quad .$$

Substitution of equations 144 and 147 into equation 143 and a straightforward integration yield:

$$\Gamma_2^{(11)} = \frac{e^{-\alpha\eta}}{x_1^{(1)}} \left[ \alpha - \frac{C'}{x_1^{(1)}} \right] . \quad (148)$$

If  $E^{(0)} \ll 1$ , which has been assumed in the previous analyses, and if also  $\beta \ll 1$ , then  $\Gamma_2^{(1)}$  can be approximated as follows:

$$\Gamma_2^{(1)} \approx e^{-\alpha\eta} \left[ \frac{\alpha(1+L\eta)}{G+F} - \frac{C'(1+2L\eta)}{(G+F)^2} \right] \quad (149)$$

where

$$L = \frac{GE^{(0)} + 2\left(\frac{\mu-1}{\mu}\right)\beta F}{G+F} .$$

The leading influence of the diffusion processes on the energy transport and temperature profile is obtained from the  $O(\epsilon)$  terms of the energy equation, which provides:

$$-\frac{d\theta^{(1)}}{d\eta} + H_{13} \Gamma_1^{(1)} + H_{23} \Gamma_2^{(1)} = E^{(1)} . \quad (150)$$

With  $\Gamma_1^{(1)}$  and  $\Gamma_2^{(1)}$  given by equations 146 and 149, respectively, the integration is straightforward. The appropriate boundary conditions are  $\theta^{(1)}(0) = \theta^{(1)}(1) = 0$ , and consequently:

$$\begin{aligned} \theta_1 = H_{13} C' \eta - H_{23} e^{-\alpha\eta} \left\{ \left[ \frac{\alpha(G+F)-C'}{(G+F)^2} \right] \frac{1}{\alpha} + \left[ \frac{\alpha(G+F)-2C'}{(G+F)^2} \right] \frac{L(1+\alpha\eta)}{\alpha^2} \right\} \\ - E^{(1)} \eta + J^{(1)} \end{aligned} \quad (151)$$

where

$$J^{(1)} = H_{23} \left\{ \left[ \frac{\alpha(G+F)-C'}{(G+F)^2} \right] \frac{1}{\alpha} + \left[ \frac{\alpha(G+F)-2C'}{(G+F)^2} \right] \frac{L}{\alpha^2} \right\}$$

and

$$E^{(1)} = H_{13}C' + H_{23} \left\{ \left[ \frac{\alpha(G+F)-C'}{(G+F)^2} \right] \frac{(1-e^{-\alpha})}{\alpha} + \left[ \frac{\alpha(G+F)-2C'}{(G+F)^2} \right] \frac{L[1 - e^{-\alpha}(1+\alpha)]}{\alpha^2} \right\} \quad (152)$$

It will be recalled that the energy transport (to  $O(\epsilon)$ ) is given by:

$$\frac{wQ}{\lambda T_o} = E^{(0)} + \epsilon E^{(1)} .$$

Two independent constants,  $G$  and  $F$ , appear in the solution. (The constant  $C'$  is related to  $G$ , equation 147.) These constants are determined by the proportions of the two chemical elements involved in the reaction. For example, assume  $A_1 = I_2$  and  $A_2 = H_2$ . If  $M_I$  and  $M_H$  are the total masses per unit volume of the elements iodine and hydrogen, respectively, in the container, the following equations must be satisfied:

$$M_I = \frac{p_o m_1}{\mathcal{R} T_o} \int_0^1 \left( x_1 + \frac{1-x_1-x_2}{2} \right) \frac{\pi}{\theta}(\eta) d\eta \quad (153)$$

$$M_H = \frac{p_o m_2}{\mathcal{R} T_o} \int_0^1 \left( x_2 + \frac{1-x_1-x_2}{2} \right) \frac{\pi}{\theta}(\eta) d\eta \quad (154)$$

These equations determine the constants  $G$  and  $F$  for the hydrogen-iodine example, and the procedure would be the same for any reaction fitting the present formalism.

No mention of rate effects has been made in this analysis, and the solution just obtained applies only in the main stream. In this respect, it

is similar to the binary solution for chemical equilibrium with  $\xi = 0$ , obtained in Section V. Because the analogy between the present problem and the binary case with regard to rate effects is so direct, and the formalism of the two cases is so similar, it is apparent that the three-component reaction exhibits the same boundary-layer behavior as the binary case; i. e. the energy transport and the composition profiles in the main stream are essentially independent of the catalytic nature of the walls when the composition is nearly in local chemical equilibrium. An analysis of rate effects for the multi-component case in general would exactly parallel the boundary layer treatment of the binary case, and none will be presented for the present example.

It is the boundary-layer character of the problem with respect to rates which makes it possible to evaluate  $G$  and  $F$  in the present example by means of equations 153 and 154, using the main-stream solution for  $x_1(\eta)$  and  $x_2(\eta)$ , and ignoring the boundary-layer behavior of the mole fractions. When the boundary layer concept is really valid, it follows that the boundary layers are very thin relative to the characteristic length of the system, as was shown in connection with the binary problem. Therefore, a negligible fraction of the total mass of the reacting mixture is contained within the boundary layers, and the boundary conditions on the mole fractions themselves, which are directly related to the total masses of various elements present, depend only on conditions in the main bulk of the mixture. With regard to this point, it may be worthwhile to repeat that although the gradients of the concentrations change rapidly in the boundary layers, the concentrations themselves remain almost constant. This was shown in the boundary layer analysis for the binary problem.

### A Numerical Example: the Hydrogen-Iodine Reaction

An example based upon reaction  $I_2 + H_2 \rightleftharpoons 2HI$  has been calculated to illustrate the features of the three-component reacting gas in equilibrium. The hydrogen-iodine reaction was chosen because (a) it meets the requirement imposed in the analysis that  $m_2/m_1$  be negligibly small, and (b) appreciable amounts of  $I_2$  and  $H_2$  are present at relatively low temperatures, i. e.  $2000^\circ K$  or less. The results, given by the perturbation treatment just discussed, are presented in figure 11. For this example the temperature at the hot wall is  $2000^\circ K$ , and at the cold wall it is  $1500^\circ K$ . It is assumed that the proportions of iodine and hydrogen in the system are such that the mole fraction of  $I_2$  at the cold wall is 75% of that at the hot wall. Formally, the dimensionless solution is independent of the pressure boundary condition,  $p_0$ , because the parameter  $\epsilon$  is determined by the temperature alone. However, the solution is actually valid only if  $p_0$  is about one atmosphere or more, because at low pressures atomic hydrogen and atomic iodine would be present in appreciable portions, and the reactions  $H_2 \rightleftharpoons 2H$  and  $I_2 \rightleftharpoons 2I$  could not be omitted from the formalism.

When there is no iodine present, the gas is composed entirely of molecular hydrogen, and the energy transport is due to ordinary thermal conduction alone. This situation, in which there can be no pressure-gradient influence, is shown by one of the curves in figure 11. Of course, if the pressure and temperature conditions were such as to permit appreciable dissociation of the  $H_2$ , the qualitative behavior would be quite different in the absence of iodine; in fact, it would then be similar to that shown for bromine dissociation in figure 5.



The second curve corresponds to a composition which is 30% molecular iodine at the hot wall. The energy transport is increased due to the diffusion mechanism, but not so extensively as in previous examples. This is because the chemical heats of formation involved in the hydrogen-iodine reaction are relatively small.

In contrast to the binary dissociation example of figure 5, the pressure gradient enhances the energy transport in the present case. This is because the diffusive energy flux is carried primarily by the heavy iodine molecules, which have the highest heat of formation in this case, rather than by the lighter molecules, as in the bromine dissociation example. The pressure diffusion mechanism tends to cause the heavier molecules to diffuse in the direction of increasing pressure, which in this case is also the direction of energy flow. It follows that if the heavier molecules make the largest contribution to the diffusive energy transport, the pressure gradient will increase the energy flux.

#### Summary: the Multi-component Gas in Local Chemical Equilibrium

The extension of the approach presented for the frozen two-component flow to cover a general multi-component gas appears to be completely straightforward. Unlike the frozen flow, the two-component gas in local chemical equilibrium is governed by a set of equations of the same order as those for a single-component gas, a feature which leads to the existence of reaction boundary layers. The manner in which this characteristic carries over to the general multi-component gas is worthy of some attention, and in this section an effort has been made to clarify this point.

Although only two examples of gases involving three components

have been considered in any detail, these examples provide a basis for a few conclusions that should apply to the multi-component case in general. The actual calculation for any number of components appears to be similar to that for three components, in principle, although not in complexity. In summarizing the discussion of the multi-component gas in equilibrium, the following remarks seem appropriate:

(a) Only in the binary reacting gas in local chemical equilibrium is the order of the system of equations the same as for one component. This feature leads to the existence of reaction boundary layers which cause the energy transport and composition profiles to be practically independent of the catalytic nature of the walls. Furthermore, the composition is completely determined in terms of the local pressure and temperature. The addition of each component beyond two, whether reacting or inert, raises the order of the set of equations by two. This does not change the boundary layer character of the solution with respect to wall-surface effects, but the composition is no longer completely determined by the local temperature and pressure. The higher order of the equations provides (or results from) the dependence of the composition and energy transport on the proportions of various chemical elements in the system.

(b) When an inert component is added to a system of reacting components in equilibrium, the qualitative behavior of the energy transport and composition profiles of the reacting species is unchanged. Instead, the effect is similar to that of shifting the pressure and temperature boundary conditions imposed on the original system of reacting components. On the other hand, two systems involving different numbers of

reacting components in equilibrium may behave quite differently, both qualitatively and quantitatively.

### VIII. CONCLUDING REMARKS

By using a simplified flow configuration and employing a perturbation technique, it has been possible to deduce with relative ease some of the principle features of energy transport in chemically-reacting gases under the influence of a pressure gradient.

When the gas is nearly chemically frozen, the energy transport depends very strongly on the degree of catalytic action provided by the walls. If the walls are completely inert, the diffusion processes make no contribution to the energy transport, which is therefore due to thermal conduction alone and independent of the pressure gradient. On the other hand, if reactions at the walls tend to drive the composition toward local equilibrium at the boundary surfaces, the energy transport is greatly increased by the diffusion flux. Under these circumstances the energy transport is a function of the pressure gradient, through the mechanism of pressure diffusion. A vortex flow operating at Mach numbers of the order of one to three, for example, might be expected to have as much as forty to fifty per cent more (or less) energy transport than a stationary gas under similar conditions, if appreciable dissociation is present. The energy flux can be either increased or decreased, depending on the reactions involved and the direction of the pressure gradient relative to the temperature gradient.

In contrast to the frozen flow, which is diffusion-dominated, the reacting gas which is nearly in local chemical equilibrium is characterized by energy transport which is practically independent of the catalytic nature of the walls. In this case the flow is reaction-dominated, and wall surface effects are confined to reaction boundary layers. The energy

transport can also be a strong function of the pressure gradient in equilibrium flow, but this is partly due to the effect of the pressure (or density) on the chemical reactions, which in turn is influenced by the pressure gradient.

The perturbation technique also provides an indication of the influence of rates on the energy transport. The strongest effect is felt when the flow is nearly in chemical equilibrium and constrained by non-catalytic walls. As the reaction rate decreases relative to the diffusion rate, so that the gas departs from equilibrium, the reaction boundary layers "grow" rapidly, carrying the damping influence of the non-catalytic walls into the main stream and sharply reducing the energy transport. The rate effects are not so strongly dependent on the pressure gradient with non-catalytic walls, but are influenced by it to some extent. It is particularly interesting that with catalytic walls the rates have no effect on the dimensionless energy transport variable unless there is a pressure gradient.

Although these conclusions are largely based upon an analysis of a two-component reaction, the behavior of the multi-component frozen flow, at least, can be expected to be qualitatively similar, in general, to that of the binary frozen flow. In some respects, the general equilibrium flow is more interesting and less simple, because of the boundary layer characteristic. In the binary case, the equations which describe the flow are of the same order as for a simple gas, and this leads directly to the existence of boundary layers. It has been shown that the addition of each component beyond two to the equilibrium flow raises the order of the equations by two. The higher order does not alter the boundary layer behavior with

respect to rates, which persists with any number of components when the mixture is in chemical equilibrium. Instead, the proportions of various chemical elements present in the gas determine the additional constants provided in the solution by the higher order of the equations.

The effect of adding an inert species to a reacting system in equilibrium, with fixed temperature and pressure boundary conditions, is much the same as shifting these boundary conditions on the original system. On the other hand, two such systems containing different numbers of reacting components may exhibit very different qualitative and quantitative characteristics.

Although problems incorporating chemical reactions and diffusion processes are inherently extremely complex, the techniques of the present work have made it possible to understand many of the features of energy transport in reacting gases by employing a relatively simple analysis. To avoid unnecessary complication, the possibility of a mass flow parallel to the energy flux (e. g. through porous walls) has been excluded in the analysis. The effect of such a mass flow on the qualitative nature of the problem is usually relatively minor and is discussed briefly in Appendix B.

As a result of this study, it is evident that energy transport in high-temperature gas flows may be quite sensitive to the pressure gradient. This effect will require careful consideration in many applications of current and future interest in the field of gasdynamics.

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# NOMENCLATURE

Following the definitions of symbols, the equation(s) in which the symbol is first used and/or defined is referenced in parentheses, when appropriate.

The superscript (i) attached to any symbol, where "i" is an integer, designates the term of order "i" in a single-parameter expansion of the quantity represented by that symbol; similarly, the superscript (ij) designates the term of order "i" in the first parameter and of order "j" in the second parameter in a two-parameter expansion.

The symbol  $O(A)$  means "of the order of A".

An underscored symbol represents a vector.

An overscored symbol represents a mean value.

A	chemical affinity (31); integration constant (used repeatedly)
$A_i$	abstraction for the chemical formula of any molecule appearing in a reaction equation (15, 36, 114, 117)
$a_i$	ratios of diffusion coefficients, treated as equal to one (112, 113)
B	integration constant (used repeatedly)
C, C'	integration constant (used repeatedly)
$C_i$	integration constant (used repeatedly)
$\bar{c}$	mean thermal speed of particles (19)
$\bar{C}_p$	mean specific heat at constant pressure of mixture (41)
$C_{p_i}$	specific heat at constant pressure of species i
$\mathcal{D}_{ij}$	multi-component diffusion coefficient (10)
$D_{ij}$	binary diffusion coefficient (12)
E	dimensionless energy eigenvalue corresponding to total energy flux = $wQ/\lambda T_0$ (41)

$E_A$	activation energy in Arrhenius law (44)
$e$	thermodynamic specific internal energy of the gas (9)
$\mathcal{F}$	body force, i. e. mass-proportional force (17)
$F, F^{(ij)}$	integration constant (used repeatedly)
$F_j$	total external force per unit mass acting on species $j$ (8)
$f_j$	Boltzmann distribution function for species $j$ (1)
$G, G^{(ij)}$	integration constant (used repeatedly)
$g_i$	a function of the distribution function of $f_j$ (1)
$H$	enthalpy parameter in binary case = $(h_1 - \frac{m_1}{m_2} h_2)Le/\bar{C}_p T_o$ (41)
$H_{ij}$	enthalpy parameter in three-component case = $(h_i - \frac{m_i}{m_j} h_j)Le/\bar{C}_p T_o$ (111)
$\Delta H_{f_i}$	standard chemical heat of formation at 298.16°K and 1 atm. (41)
$h_i$	partial specific enthalpy of species $i$ = $\Delta H_{f_i}(T_1) + \int_{T_1}^{T_2} C_{p_i} dT$ (14, 41)
$J$	"flux" in the formalism of irreversible thermodynamics (25)
$J^{(ij)}$	integration constant (used repeatedly)
$K_j$	rate of production (moles/cm <sup>3</sup> -sec) of species $j$ (5, 16)
$K_n$	equilibrium constant expressed in terms of concentrations (46)
$k$	Boltzmann's constant (14)
$k_b$	backward (reverse) reaction rate (16)
$k_f$	forward reaction rate (16)
$Le$	Lewis number = $\bar{C}_p nD_{12}/\lambda$ (41)
$L_{ik}$	"phenomenological coefficient" in the formalism of irreversible thermodynamics (25)
$M$	molecular weight of "heavy" species (18) ; Mach number (37)

$M_{A_2}$	total mass per unit volume of species $A_2$ in system (122)
$M_H$	total mass per unit volume of element hydrogen in system (154)
$M_I$	total mass per unit volume of element iodine in system (153)
$m$	molecular weight of "light" species (22); temperature exponent (46)
$\dot{m}$	mass flow
$m_{A_2}$	molecular weight of species $A_2$ (122)
$m_j$	molecular weight of species $j$ (6)
$n$	total concentration (moles/cm <sup>3</sup> ) of the mixture (10)
$n_j$	concentration (moles/cm <sup>3</sup> ) of species $j$ (5)
$n_o$	total concentration (moles/cm <sup>3</sup> ) at hot wall ( $\eta = 0$ ) (46)
$P$	pressure (stress) tensor (2, 13)
$p$	static or thermodynamic pressure (11)
$p_o$	static pressure at hot wall ( $\eta = 0$ ) (38)
$Q$	energy flux vector (3, 14)
$\mathcal{R}$	universal gas constant in perfect gas equation of state (45)
$R$	rate parameter = $(w^2 k_b n^3 / n D_{12})_{\eta=0}$ (46, 47)
$r$	independent variable (length) (38)
$r_o$	radius of inside cylinder of a concentric pair (37)
$s$	specific entropy (27)
$s_i$	specific entropy associated with irreversible entropy production alone (26)
$s_k$	partial specific entropy associated with species $k$ (35)
$T$	temperature (10)
$T_o$	temperature at hot wall in channel flow ( $\eta = 0$ ) (41)
$T_1$	temperature at cold wall in channel flow ( $\eta = 1$ )

U	velocity component of mixture parallel to temperature gradient
$u_j$	diffusion velocity (4, 10)
V	tangential velocity component of mixture in cylindrically-symmetric flow
$V_j$	mean velocity of species j relative to fixed coordinate system (4)
$V_o$	mass average velocity = $1/\rho \sum_j m_j V_j$
$v_k$	partial specific volume associated with species k (35)
w	channel width in channel-flow approximation (37)
$X_k$	"force" in the formalism of irreversible thermodynamics (25)
x	mole fraction of atomic species in binary case = $n_1/n$ (42)
$x_i$	mole fraction of species i = $n_i/n$ (108)
Y	abstraction for the chemical formula of the third body in recombination (43)
y	extent of departure from local equilibrium by $x^{(10)}$ in reaction boundary layer (102)
Z	"frequency factor" in Arrhenius law (44)
z	appropriate independent variable in reaction boundary layer = $\eta/\xi^{\frac{1}{2}}$ (94a)
$\alpha$	dimensionless parameter used to characterize temperature behavior of equilibrium constant = $\theta_a E^{(o)}$ (54)
$\alpha_i$	thermal diffusion constant (10)
$\beta$	dimensionless parameter which characterizes pressure gradient (37, 38)
$\Gamma$	dimensionless diffusion flux of atomic species in binary case = $w n_1 u_1 / n D_{12}$ (41, 42)
$\Gamma_i$	dimensionless diffusion flux of species i in three-component case = $w n_i u_i / n D_{12}$ (111, 112, 113)

$\gamma$	mean specific heat ratio = $\overline{C_p}/\overline{C_v}$ (37)
$\delta$	dimensionless expansion parameter in perturbation analysis (48, 56)
$\epsilon$	dimensionless expansion parameter in perturbation analysis (48, 53; 139)
$\eta$	dimensionless independent variable = $r-r_o/w$ (38)
$\theta$	dimensionless temperature variable = $T/T_o$ (41)
$\theta_a$	dimensionless activation energy = $E_A/kT_o$ (55)
$\lambda$	coefficient of thermal conductivity (14)
$\mu$	coefficient of viscosity (13) ; molecular weight ratio $m_3/m_1$ (112)
$\mu_i$	chemical potential of species i (29, 35)
$\nu$	expansion parameter in three-component analysis (120)
$\nu_j^g$	stoichiometric coefficient of species j in reaction g (15)
$\xi$	dimensionless expansion parameter in perturbation analysis (85, 86)
$\pi$	dimensionless pressure variable = $p/p_o$ (38)
$\rho$	mass density (mass per unit volume) (7)
$\sigma$	expansion parameter in Chapman-Enskog solution to Boltzmann equation; effective collision cross section (19)
$\tau$	stoichiometric coefficient in binary reaction (155)
$\phi_i$	see figures
$\psi_i$	see figures
$\omega_j^g$	stoichiometric coefficient of species j in reaction g

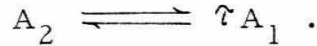
## APPENDIX A

### The Generalized Fourier Heat Conduction Law for the Binary Reacting Gas in Chemical Equilibrium

When a reacting gas mixture of two components is very nearly in chemical equilibrium, the concentrations are related by the equilibrium constant:

$$\frac{n_1^{\tau}}{n_2} = K_n(T) \quad (155)$$

where  $n_1$  and  $n_2$  are the concentrations of species  $A_1$  and  $A_2$ , respectively, and the reaction is represented symbolically by:



Since  $n_1 = xn$  and  $n_2 = (1-x)n$ , where  $n$  is the total concentration:

$$\frac{x^{\tau}}{1-x} = \frac{K_n(T)}{n^{\tau-1}} . \quad (156)$$

The molecular weight ratio  $m_2/m_1 = \tau$ , and the density  $\rho = n \bar{m} = n [xm_1 + (1-x)m_2]$ , so the diffusion equation obtained from equations 11 and 12 can be written:

$$u_2 - u_1 = D_{12} \left[ \frac{1}{x(1-x)} \nabla x - \left( \frac{1 - \tau}{\tau(1-x) + x} \right) \frac{1}{p} \nabla p \right] . \quad (157)$$

The mole fraction  $x$  is a function of pressure and temperature, so that:

$$\nabla x = \left( \frac{\partial x}{\partial T} \right)_p \nabla T + \left( \frac{\partial x}{\partial p} \right)_T \nabla p . \quad (158)$$

If the mixture obeys the perfect gas law,  $p = n \mathcal{R} T$ , then according to equation 156:

$$\left(\frac{\partial x}{\partial p}\right)_T = \left[ \frac{x(1-x)}{\bar{r}(1-x)+x} \right] \frac{(1-\bar{r})}{p} . \quad (159)$$

When equations 157, 158 and 159 are combined, the pressure gradient terms cancel, and the diffusion equation becomes:

$$u_2 - u_1 = D_{12} \left[ \frac{1}{x(1-x)} \left(\frac{\partial x}{\partial T}\right)_p \right] \nabla T . \quad (160)$$

Since  $xm_1u_1 + (1-x)m_2u_2 = 0$  (according to equation 39), the energy flux given by equation 14 can be written:

$$Q = - \left\{ \lambda + nD_{12} \frac{(\bar{r}h_1 - h_2)\left(\frac{\partial x}{\partial p}\right)_T}{x(1-x)[\bar{r}(1-x)+x]} \right\} \nabla T . \quad (161)$$

The mole fraction  $x$  and  $(\partial x/\partial p)_T$  can be obtained in terms of pressure and temperature from equation 156. Therefore, when the binary mixture is very nearly in chemical equilibrium, the energy flux can be described by a generalized Fourier equation, where the effective coefficient of thermal conductivity includes the effects of chemical reactions and diffusive transport and is a function of the local pressure and temperature.

## APPENDIX B

### The Influence of a Mass Flow Through the System

In some of the gasdynamic applications in which the mechanisms studied here are important, such as the vortex containment device for the fission rocket, there is the possibility of a mass flow parallel to the temperature gradient, through the use of porous walls or by other injection techniques. Such a convection current may have a very considerable quantitative influence on the energy transport. For example, when there is appreciable dissociation in the gas (e. g. 30 per cent at the hot wall), even a relatively small mass flow, with a velocity  $U$  parallel to the temperature gradient of the same order as the diffusion velocities, may change the energy transport by roughly a factor of two compared with that in the absence of convection (10). The mathematical complexity of the present investigation has been reduced somewhat by excluding the possibility of convection through the walls, primarily because the qualitative nature of the associated effects is relatively easy to understand.

The convective mass flow carries with it the thermodynamic enthalpy and chemical heat of formation of the various species, and in this way transports energy. The mechanism is very similar to that of diffusion; in fact, the convection simply adds a velocity component  $\pm U$  to each of the diffusion velocities, so that it tends to either augment or counteract the influence of diffusion, depending on the direction of the mass flow. Ordinarily the convection does not change the qualitative behavior of the energy transport, but merely alters the magnitude. This is because in most applications of interest the convective velocity  $U$  is



practically independent of the pressure gradient and concentration gradients, unlike the diffusion velocities, and the latter therefore predominate in dictating the qualitative behavior. Of course, the velocity  $U$  is related to the local concentrations through the continuity equation, i. e.

$$U = \frac{\dot{m}}{n \sum x_i m_i}$$

where  $\dot{m}$  is the mass flow per unit area. Therefore, the effect of the convection is not usually as straightforward as if a constant  $U$  were superimposed upon the diffusion velocities. It should also be mentioned that the velocity component  $U$  is related to the pressure gradient through the momentum equation, but in most practical applications other velocity components are so much greater than  $U$  that this coupling is unimportant. For example, in the previously mentioned vortex applications, the tangential velocity  $V \gg U$ , and the radial equation of motion is practically independent of  $U$ , i. e.:

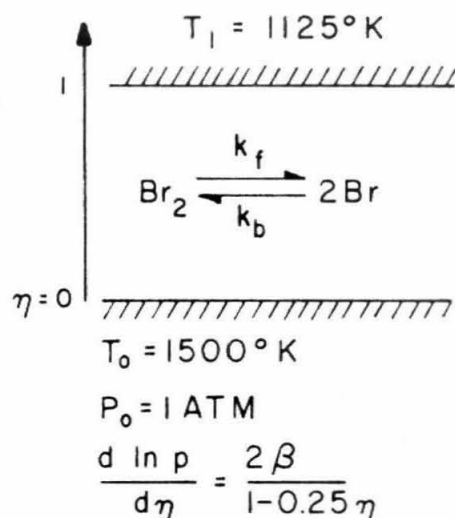
$$\frac{dp}{dr} \approx \rho \frac{V^2}{r} .$$

When the coupling between  $U$  and the pressure gradient is not negligible, convection will ordinarily be the predominating mechanism of energy transport, and the qualitative and quantitative effects of diffusive transport will be relatively unimportant.

The presence of a mass flow through the walls also changes the manner in which boundary conditions are applied. In the previous section it was shown that with the addition of each component beyond one in frozen flow, or beyond two in chemical-equilibrium flow, the order of the set of equations is raised by two. This is true whether or not there is convection. It was demonstrated that the solution can be put in a form such that

the constants which follow from the higher order of the equations correspond to the mole fractions of the various species at an arbitrary point, e.g. at one wall. When there is no mass flow, these constants are determined by the total masses of the various chemical elements in the system, through expressions such as equations 153 and 154. On the other hand, when there is a mass flow through the system, the constants are evaluated by specifying the mass flows of the various species. For example, the mole fraction of species  $j$  is clearly proportional to the mass flow of  $j$ , i.e.  $\dot{m}_j = x_j n(U + u_j)$ . The presence of convection does not alter the boundary layer behavior with respect to the catalytic action of the walls, which is always associated with chemical-equilibrium flow. In the binary gas in local equilibrium the profiles are completely determined in terms of the pressure and temperature, just as with no convection, and specifying the mass flux fixes the pressure at some arbitrary point.

ENERGY TRANSPORT IN CHEMICALLY FROZEN OR NEAR-FROZEN CHANNEL-TYPE FLOW OF BROMINE WITH 30% DISSOCIATION AT THE HOT WALL WHEN WALL IS CATALYTIC.



CATALYTIC WALLS:  $\frac{wQ}{\lambda T_0} = \phi_1 - \delta \phi_3$

NON-CATALYTIC WALLS:  $\frac{wQ}{\lambda T_0} = \phi_2 + \delta \phi_4$

$$\delta = \left( \frac{K_n^{1/2} k_b w^2 n^{3/2}}{D_{12}} \right)_{\eta=0} \sim \frac{\text{REACTION RATE}}{\text{DIFFUSION RATE}}$$

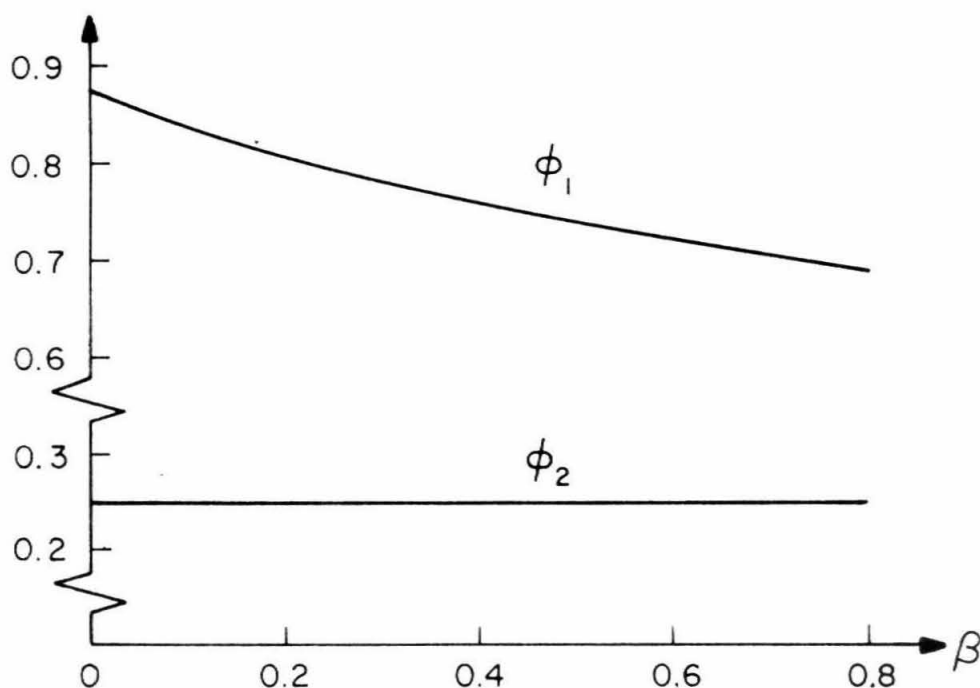
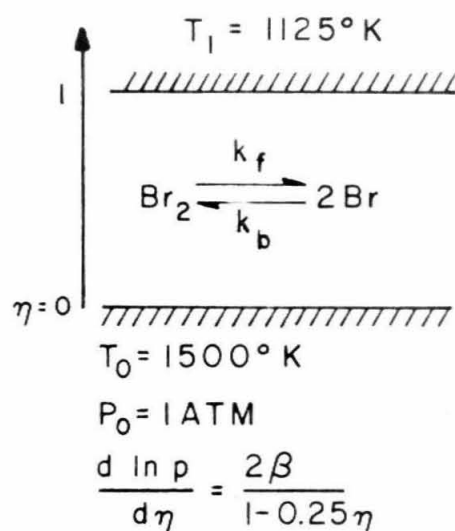


FIGURE 1. COMPLETELY FROZEN FLOW

ENERGY TRANSPORT IN CHEMICALLY FROZEN OR NEAR-FROZEN CHANNEL-TYPE FLOW OF BROMINE WITH 30% DISSOCIATION AT THE HOT WALL WHEN WALL IS CATALYTIC.



CATALYTIC WALLS:  $\frac{wQ}{\lambda T_0} = \phi_1 - \delta \phi_3$

NON-CATALYTIC WALLS:  $\frac{wQ}{\lambda T_0} = \phi_2 + \delta \phi_4$

$$\delta = \left( \frac{K_n^{1/2} k_b w^2 n^{3/2}}{D_{12}} \right)_{\eta=0} \sim \frac{\text{REACTION RATE}}{\text{DIFFUSION RATE}}$$

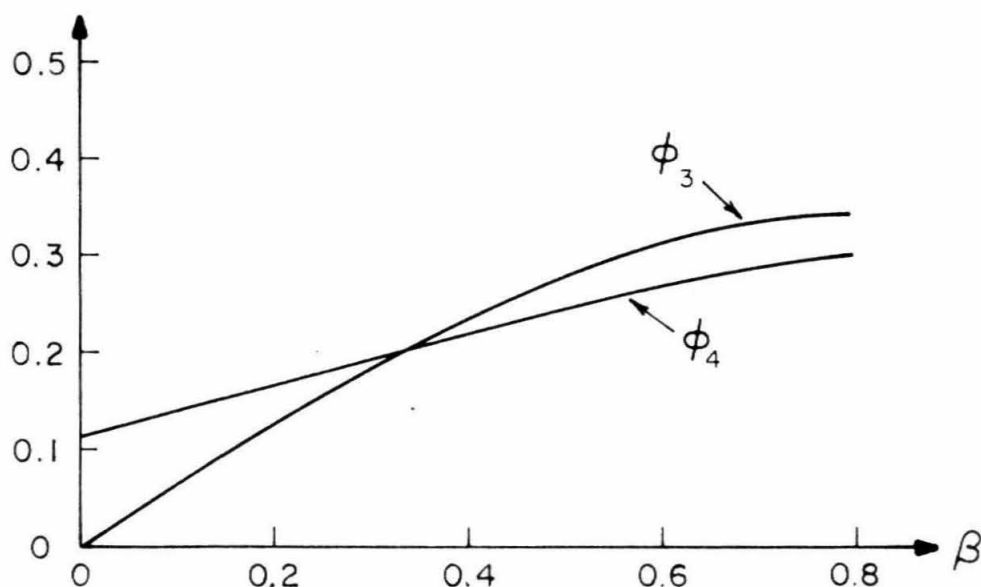


FIGURE 2. INFLUENCE OF REACTION RATE/DIFFUSION RATE

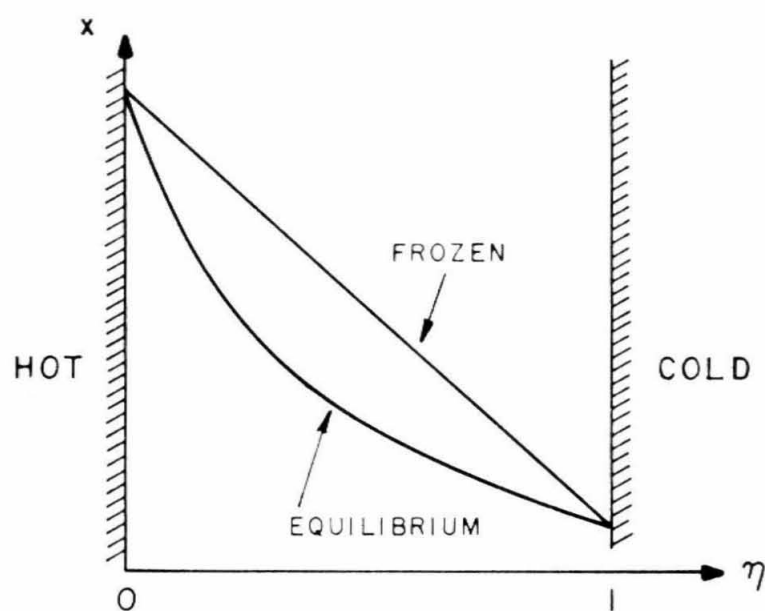


FIGURE 3. DISTRIBUTION OF ATOMIC MOLE FRACTION  $x$  WITH CATALYTIC WALLS

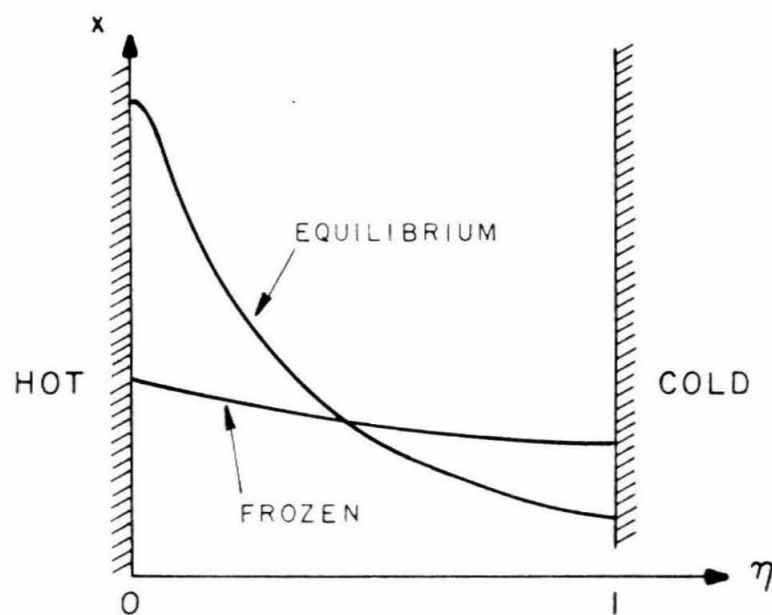
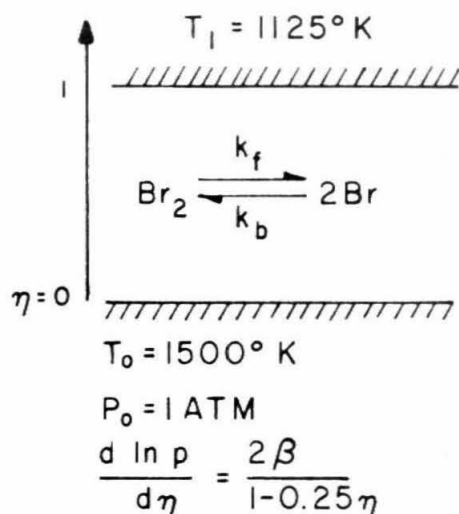


FIGURE 4. DISTRIBUTION OF ATOMIC MOLE FRACTION  $x$  WITH NON-CATALYTIC WALLS

ENERGY TRANSPORT IN CHEMICAL EQUILIBRIUM OR NEAR-EQUILIBRIUM CHANNEL-TYPE FLOW OF BROMINE WITH 30% DISSOCIATION AT THE HOT WALL.



CATALYTIC WALLS:  $\frac{wQ}{\lambda T_0} = \psi_1 - \xi \psi_2$

NON-CATALYTIC WALLS:  $\frac{wQ}{\lambda T_0} = \psi_1 - \xi^{1/2} \psi_3 + \xi \psi_4$

$$\xi = \left( \frac{D_{12}}{K_n^{1/2} k_b w^2 n^{3/2}} \right)_{\eta=0} \sim \frac{\text{DIFFUSION RATE}}{\text{REACTION RATE}}$$

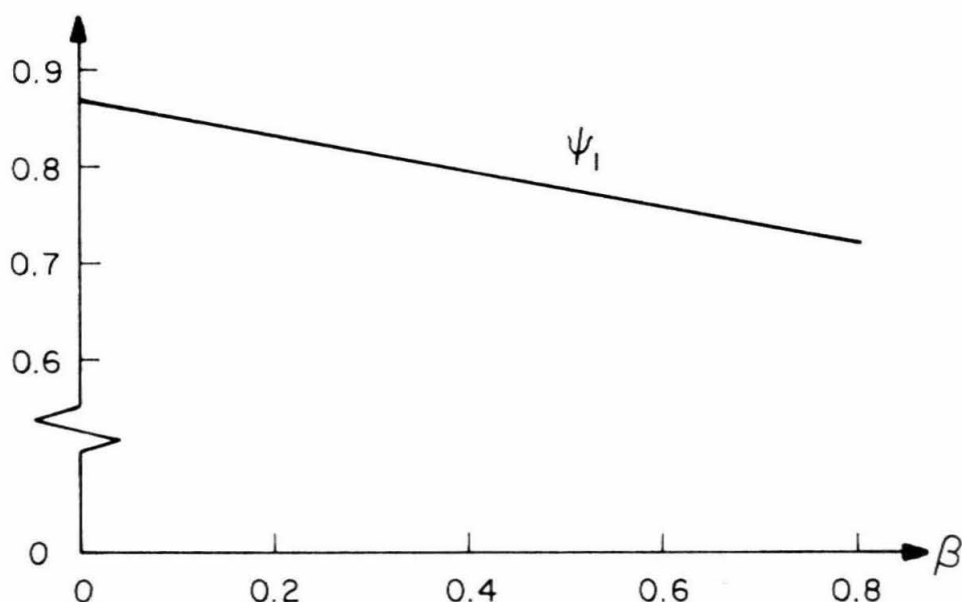
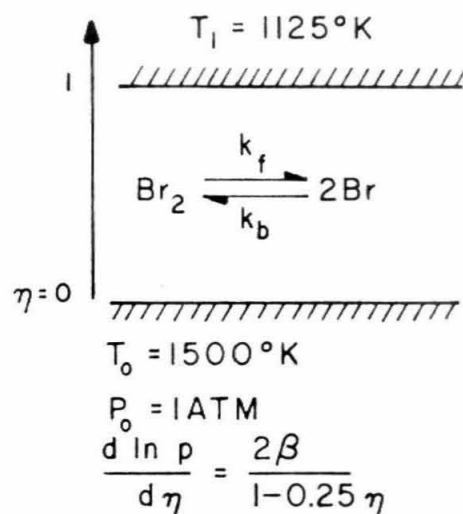


FIGURE 5. FLOW COMPLETELY IN EQUILIBRIUM, WITH CATALYTIC OR NON-CATALYTIC WALLS

ENERGY TRANSPORT IN CHEMICAL EQUILIBRIUM OR NEAR-EQUILIBRIUM CHANNEL-TYPE FLOW OF BROMINE WITH 30% DISSOCIATION AT THE HOT WALL.



CATALYTIC WALLS:  $\frac{wQ}{\lambda T_0} = \psi_1 - \xi \psi_2$

NON-CATALYTIC WALLS:  $\frac{wQ}{\lambda T_0} = \psi_1 - \xi^{1/2} \psi_3 + \xi \psi_4$

$$\xi = \left( \frac{D_{12}}{K_n^{1/2} k_b w^2 n^{3/2}} \right)_{\eta=0} \sim \frac{\text{DIFFUSION RATE}}{\text{REACTION RATE}}$$

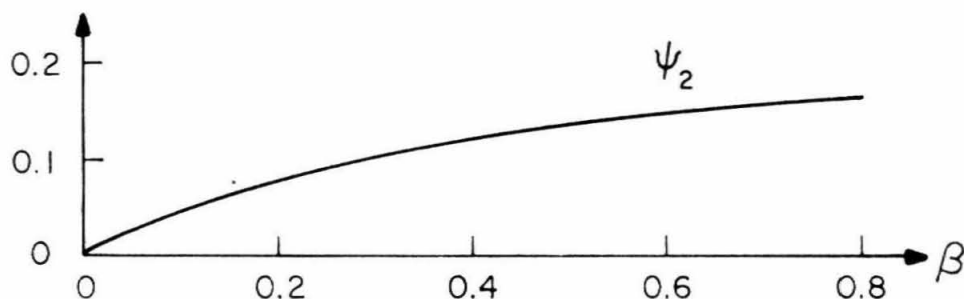
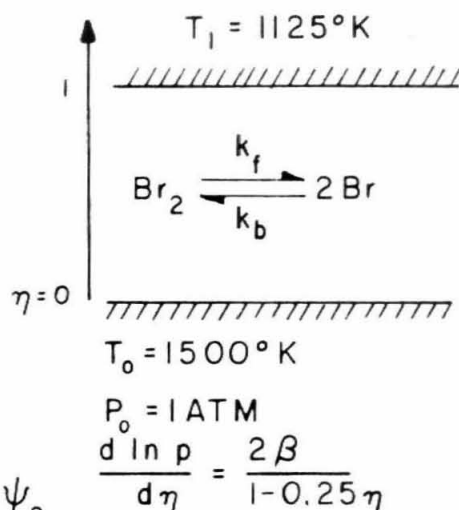


FIGURE 6. INFLUENCE OF DIFFUSION RATE/REACTION RATE WITH CATALYTIC WALLS

ENERGY TRANSPORT IN CHEMICAL  
EQUILIBRIUM OR NEAR-EQUILIBRIUM  
CHANNEL-TYPE FLOW OF BROMINE  
WITH 30% DISSOCIATION AT THE  
HOT WALL.



CATALYTIC WALLS:

$$\frac{wQ}{\lambda T_0} = \psi_1 - \xi \psi_2$$

NON-CATALYTIC WALLS;  $\frac{wQ}{\lambda T_0} = \psi_1 - \xi^{1/2} \psi_3 + \xi \psi_4$

$$\xi = \left( \frac{D_{12}}{K_n^{1/2} k_b w^2 n^{3/2}} \right)_{\eta=0} \sim \frac{\text{DIFFUSION RATE}}{\text{REACTION RATE}}$$

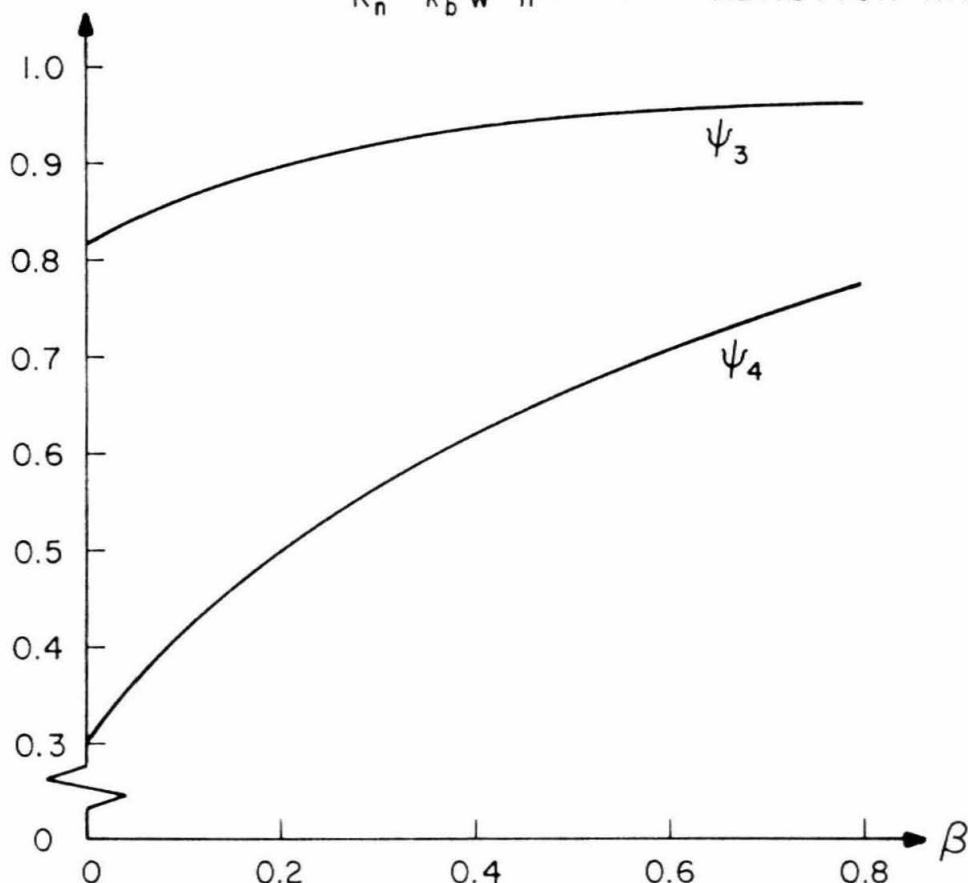
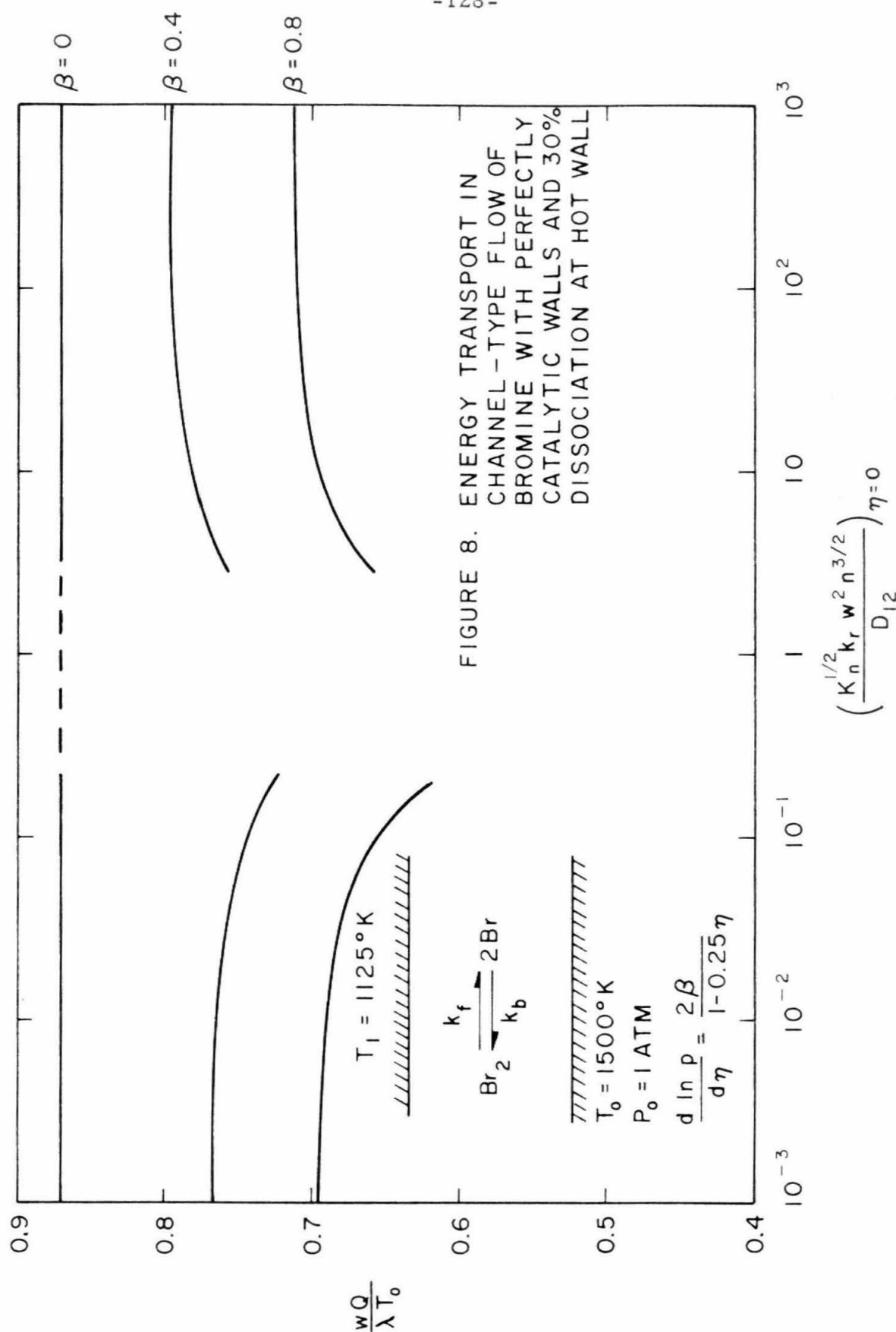
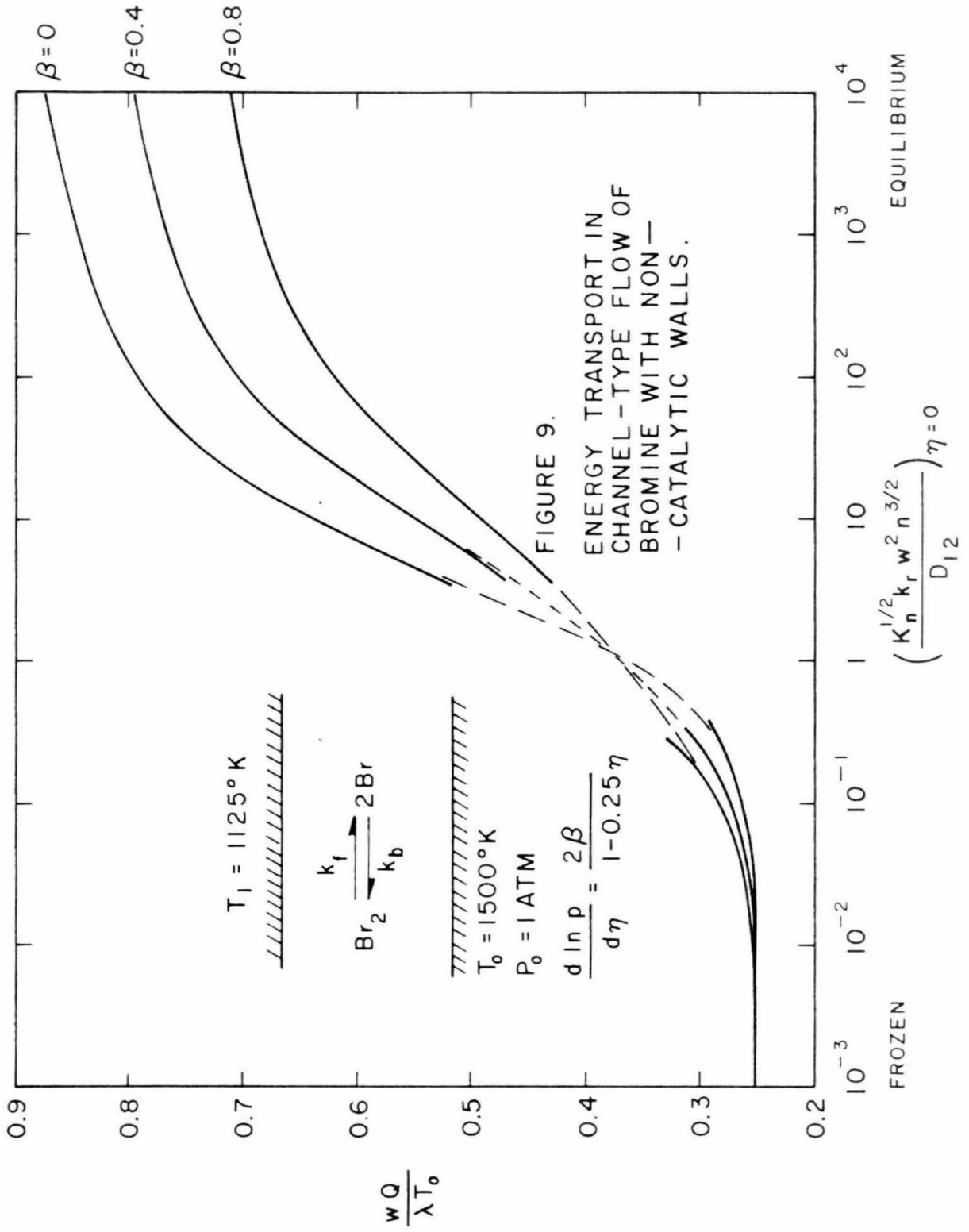


FIGURE 7. INFLUENCE OF DIFFUSION RATE/REACTION RATE  
WITH NON-CATALYTIC WALLS







# ENERGY TRANSPORT IN CHANNEL-TYPE EQUILIBRIUM FLOW OF DISSOCIATING BROMINE IN THE PRESENCE OF ARGON

$$\frac{wQ}{\lambda T_0} = \psi_1 - \nu \psi_5$$

$\nu$  = Mole fraction of argon at hot wall

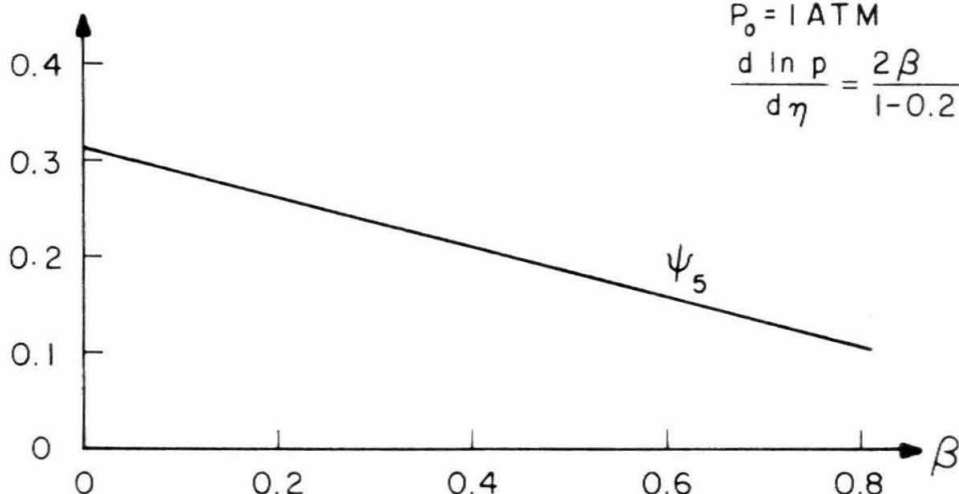
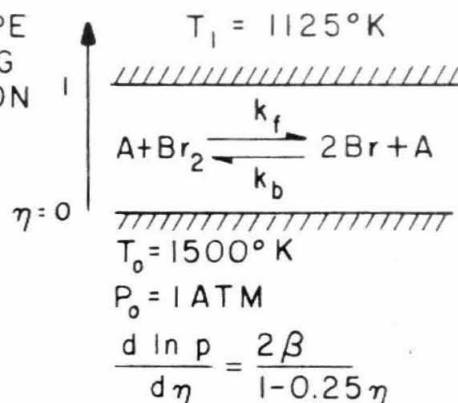


FIGURE 10.

# ENERGY TRANSPORT IN CHANNEL-TYPE EQUILIBRIUM FLOW OF HYDROGEN AND IODINE

Mole fraction of  $I_2$  at both walls is fixed by masses of I and H in system. It is assumed  $X_{I_2}(\eta=1)/X_{I_2}(\eta=0) = 0.75$

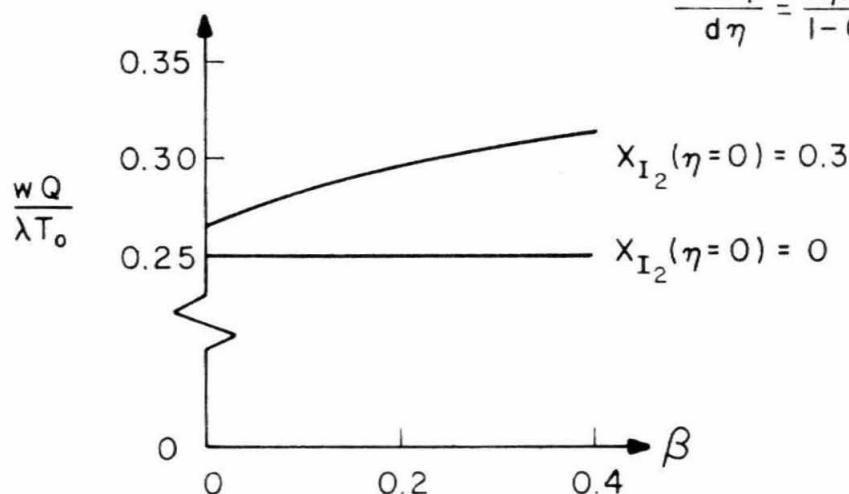
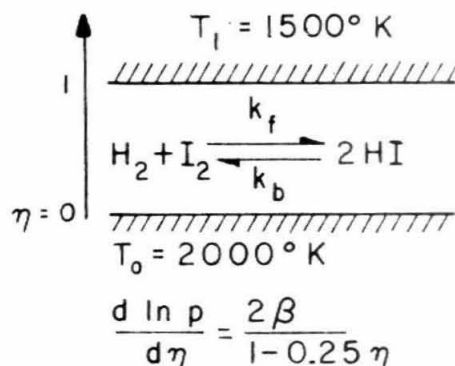


FIGURE 11.